Vol. XXVI. [MAY, 1904.] No. 5.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

ON THE OXYGEN ETHERS OF UREA.

BY W. M. BRUCE.

Received February 6, 1904.

(Continued from p. 436.)

II. CONDENSATIONS OF THE ISOUREAS.

Sym. O-Methyl Diphenyldiureidoisourea,
$C_6H_5NHCONHC(OCH_3):NCONHC_6H_5$.

—Methyl phenylisobiuret, 0.6 gram, prepared according to the method of Stieglitz and McKee, was treated with 0.3 gram phenylisocyanate, the material being kept cold. The product soon became semi-fluid and after standing over night the contents of the tube had become solid. This solid was washed a great many times with ether and then melted constant at 153°. It gave: C, 61.60; H, 5.46. Calculated: C, 61.47; H, 5.18.

Some of the above compound was dissolved in absolute ether and treated with a little dry hydrogen chloride. The precipitate was filtered off, washed with absolute ether and dried as usual for one and a half hours. The salt melted at 122°, giving off methyl chloride. A chlorine determination gave results agreeing best

with a sesquichloride. There was found 14.81 per cent. Cl. Calculated for $(C_{16}H_{16}O_3N_4)_2.3HCl$, 14.48 per cent.

Carbonyl Diphenyldiurea, $(C_6H_5NHCONH)_2CO$.—Some of the diureïd was placed in a sample tube and treated with dry hydrogen chloride at 60°. Methyl chloride was evolved and a colorless solid was left which melted sharply at 211°. As the quantity was small, the substance was placed in a desiccator for a day or two and then analyzed without further purification. It gave: C, 60.50; H, 5.20. Calculated: C, 60.34; H, 4.74.

O-Methyl Carbethoxyisourea, $C_2H_5OCONC(OCH_3)NH_2$.—Methyl isourea hydrochloride, 2 grams, was treated at 0°, in ethereal solution with potassium hydroxide (2.2 grams dissolved in 1.5 cc. water) and ethyl chlorformate (1.9 gram). The dried ether extracts left a colorless mobile oil, which, when it was cooled in a freezing-mixture and persistently scratched, solidified completely. The substance was purified by precipitation from ether solution by petroleum ether. The melting-point is 5°. The analysis gave: C, 41.15; H, 7.21. Calculated: C, 41.05; H, 6.91.

O-Methyl Carbethoxyisourea Hydrochloride,

$$C_2H_5OCONC(OCH_3)NH_2.HCl.$$

—Some methyl carbethoxyisourea was dissolved in absolute ether and dry hydrogen chloride passed into the solution. The precipitate was filtered off, washed and dried as usual and analyzed (I, II and III) after an interval of half an hour and again (IV) after a week. There was found, I, 17.72, II, 18.02, III, 19.16, and IV, 15.15 per cent. Cl. Calculated, 19.40 per cent.

These results show a gradual decomposition with loss of chlorine. The decomposition occurs as follows:

$$C_2H_5OCONC(OCH_3)NH_2.HCl \rightarrow CH_3Cl + C_2H_5OCONHCONH_2.$$

This was confirmed by the following: Some methyl carbethoxyisourea was treated with dry hydrogen chloride; at the ordinary temperature, methyl chloride was evolved. The solid residue was washed with water and dried; it then melted at 191° and was recognized as allophanic ester.

Some of the hydrochloride, when heated, evolved methyl chloride in quantity at 90°.

All attempts to introduce a second carbethoxyl group left the body unchanged.

O-Methyl Thiophenylureidoisourea, $(C_6H_5NHCSN:)C(OCH_3)NH_2$.—Methyl isourea, 0.2 gram, was mixed with 0.5 gram phenyl mustard oil; heat was evolved and the product soon solidified when it was cooled. The substance was purified by several recrystallizations from hot benzene. Obtained thus, the compound consists of diamond-shaped plates, insoluble in water and ether but easily soluble in chloroform. The melting-point is 131°.

The compound can also be obtained much more conveniently by warming the isourea hydrochloride with phenyl mustard oil and potassium hydroxide in the presence of a little water. The yield, however, is much less by this method.

The substance is somewhat unstable. When kept in a desiccator several days it melted at 121°-126° and on analysis (I) gave a low nitrogen content. Another sample (II) was analyzed after remaining in a vacuum only two hours. The results were 19.04 and 19.92 per cent. N. Calculated, 20.13 per cent.

Methyl phenylisothiobiuret was dissolved in chloroform and dry hydrogen chloride added. The white crystalline precipitate was dried and when heated to 115° melted with evolution of methyl chloride.

Methyl phenylisothiobiuret, when treated with dry hydrogen chloride and heated to 75°-90°, gave off methyl chloride. The solid phenylthiobiuret remaining in the tube was recrystallized from absolute alcohol and obtained in the form of very fine needles, which melted at 171° with decomposition, a gas being evolved having an odor similar to that of mercaptan.

While methyl isourea condenses with 2 molecules of phenylisocyanate, it reacts only with 1 molecule of phenyl mustard oil.

O-Methyl Isobiuret, $H_2NCON:C(OCH_3)NH_2$.—One gram methyl isourea hydrochloride was dissolved in 4 cc. water and added to a solution of 0.08 gram potassium isocyanate in 4 cc. water and the mixture allowed to evaporate to dryness in a warm place. The residue was extracted repeatedly with boiling benzene. The benzene solution was evaporated and 0.2 gram of a solid was obtained which melted at 110°. Some of this solid, when treated with dry hydrogen chloride, began to evolve methyl chloride at the room temperature and left a product which, thoroughly washed with water and dried, melted at 190°—the melting-point of

biuret. It also gave the biuret reaction with copper sulphate and sodium hydroxide. Methyl isobiuret, when purified by recrystallization from hot benzene, melted at 118°.

The analysis gave: C, 30.98; H, 6.30. Calculated: C, 30.72; H, 6.03.

Benzylidene Dimethyldiisourea,

$$C_6H_5CH:(NHC(OCH_3):NH)_2.$$

—Methyl isourea, 0.72 gram, was added to 1 gram (a mol.) benzaldehyde. Nearly all the methyl isourea dissolved in a few minutes without heat evolution. After standing for about two days, the substance was almost completely solid. This solid, insoluble in ether, acetone and chloroform but soluble in methyl alcohol, was washed many times with absolute ether. It then melted constant at 137°. The ether washings were treated with dry hydrogen chloride and allowed to stand and a small amount of a crystalline substance separated which melted at 235°. Tribenzotetraureïd melts at 240°.

The substance melting at 137° was analyzed and gave: C, 55.33; H, 6.81. Calculated: C, 55.85; H, 6.84.

It is evident from the above that 2 molecules of methyl isourea reacted with one of the benzaldehyde as follows:

$$2H_2NC(OCH_3):NH + C_6H_5CHO \rightarrow C_6H_5CH:[NHC(OCH_3):NH]_2 + H_2O.$$

Small quantities of a tribenzylidene tetraisourea were formed at the same time.

Some of the diisourea when treated with dry hydrogen chloride evolved methyl chloride at the room temperature. The residue, benzylidene diureïd, was washed with ether and acetone and began to decompose when heated to 195°-200° and melted at 210°, giving off a little gas. Schiff[1] gives the melting-point of his benzodiureïd as 195° and adds that heated higher it decomposed. Richter gives the melting-point 200°.

The following experiment was made in the attempt to obtain the hydrochloride. The isodiureïd was dissolved in absolute methyl alcohol and dry hydrogen chloride slowly passed into the cold solution. A precipitate, obtained by the addition of ether, was filtered off, washed and dried as usual for two hours.

It then melted at 85°, giving off methyl chloride. It gave, by

[1] *Ann. Chem.* (Liebig), **151**, 192 (1869).

titration, 19.37 per cent. Cl. Calculated for $C_{11}H_{16}O_2N_4.2HCl$, 22.91 per cent.

Benzylidene Diethyldiisourea,

$$C_6H_5CH:[NHC(OC_2H_5):NH]_2.$$

—Ethyl isourea, 0.7 gram, dissolved in a little absolute ether, was mixed with 0.84 gram (1 mol.) redistilled benzaldehyde. After standing two weeks, a white crystalline mass was obtained which was thoroughly washed many times with absolute ether and finally with a little acetone. The substance then melted at 154° and was insoluble in water, ether and alkalies and nearly insoluble in benzene, but soluble in chloroform, acetone and in dilute acids. No definite crystalline form could be observed under the microscope.

The analysis gave: C, 59.19; H, 7.51. Calculated: C, 59.01; H, 7.64.

An impure hydrochloride of the isodiureïd was obtained by treating a chloroform solution of the ureïd with dry hydrogen chloride. When heated, this salt melted and gave off ethyl chloride at 90°. The chloride was allowed to stand in the air in a warm place for several hours. The melting-point was then found to be 195°—the melting-point of benzodiureïd. Evidently complete decomposition had occurred.

Some ethyl isourea and benzaldehyde were mixed in equimolecular quantities and the mixture allowed to stand for several months. The product was then washed with ether and treated with dry hydrogen chloride. Ethyl chloride was evolved and a solid residue remained which, when purified, melted at 240° with decomposition. This is the melting-point tribenzylidene tetraureïd. Evidently the substance formed by the long-continued action of benzaldehyde was a much higher condensation product than that first obtained. This substance, as is shown by its decomposition product, tribenzylidene tetraureïd, was tribenzylidene tetrethyl isotetraureïd.

By condensation of isourea ethers with β-keto-acid esters the oxygen ethers of μ-oxypyrimidines were easily obtained. Their ready formation by this method promises to be serviceable in synthetic work in the uric acid series.[1]

[1] Mr. R. W. Noble is carrying out work along this line in this laboratory.—J. S.

μ-Methoxy-α-methyl-γ-oxypyrimidine,

$$\underset{\llcorner\!\!\!

$$HCl, N : C(OCH_3)N : C(CH_3)CH : COH \rightarrow$$
$$HN, CO.N : C(CH_3)CH : COH + CH_3Cl$$

By titration there was found 20.03 per cent. Cl. Calculated, 20.06 per cent.

The silver salt was obtained from 0.2 gram of the oxypyrimidine dissolved in absolute methyl alcohol, by the addition of a methyl alcohol solution of sodium methylate (prepared from the calculated amount of sodium) and then of the equivalent amount of silver nitrate in a mixture of methyl alcohol and water (1:1). A very thick gelatinous precipitate formed which it was impossible to wash even with the pump. It was placed on a clay plate *in vacuo* for several days until it was perfectly dry, then finely powdered and washed repeatedly with water, methyl alcohol and ether, and dried as before. It thus gave 43.36 per cent. Ag. Calculated for $C_6H_7O_2N_2Ag$, 43.65 per cent.

μ-Ethoxy-α-methyl-γ-oxypyrimidine,

$$N : C(OC_2H_5).N : C(CH_3)CH : COH$$

—Ethyl isourea, 2 grams, was mixed with 3 grams (1 mol.) acetoacetic ether. The mixture, warmed at 60° for one hour, almost completely solidified. This solid, when washed with absolute ether and recrystallized from boiling absolute alcohol, was obtained in the form of fine shining needles, which melted at 206°. These gave: C, 54.43; H, 6.73. Calculated: C, 54.48; H, 6.55.

The chlorplatinate was prepared by the method described above for the corresponding methyl derivative. The crystals were yellow needles, which gave 26.95 per cent. Pt. Calculated, 27.14 per cent.

A small amount of the oxypyrimidine in concentrated benzene solution was treated with a little dry hydrogen chloride. The precipitate was washed with dry benzene and dried for forty minutes (I) and eighteen hours (II), respectively. By titration these gave, 17.49 and 17.78 per cent. Cl. Calculated for $C_7H_{10}O_2N_2HCl$, 18.59 per cent.

Some of the oxypyrimidine was heated in a stream of dry hydrogen chloride and evolved ethyl chloride at 90°-130°. The solid residue decomposed when heated to 270°. It was methyl uracil.

μ-Methoxy-α-methyl-β-ethyl-γ-oxypyrimidine,

$$N:C(OCH_3).N:C.(CH_3).C(C_2H_5)C\ OH.$$

—Methyl isourea, 0.6 gram, was mixed with 1.2 grams (1 mol.) ethyl acetoacetic ether. The mixture formed a clear oil which on standing over night became filled with four-sided needles in masses from a common center. The crystals were washed with absolute ether and after several recrystallizations from hot absolute alcohol melted constant at 210°.

The compound is easily soluble in acid or alkali. The analysis gave: C, 56.94; H, 7.43. Calculated: C, 57.07; H, 7.20.

An attempt was made to prepare the hydrochloride from the oxypyrimidine in benzene or chloroform solution and dry hydrogen chloride, but the product was always mucilaginous and not easily purified. However, the salt was easily obtained from a solution of 0.3 gram oxypyrimidine in the calculated amount of hexanormal hydrochloric acid, by evaporation *in vacuo*. After standing *in vacuo* nearly a day the dry salt was analyzed, and gave 17.12 per cent. Cl. Calculated for $C_8H_{13}O_2N_2Cl$, 17.31 per cent.

O-Methyl Oxalylisourea, (μ-Methyl Parabanic Acid),

$$NH.C(OCH_3):N.CO.CO.$$

—Methyl isourea, 0.4 gram, was mixed with a slight excess (1 gram) oxalic ester. In a few minutes the whole mass apparently became solid. After standing for several days, the compound was washed repeatedly with ether, benzene and petroleum ether and then recrystallized from absolute alcohol. It was obtained in the form of three-sided prisms, which melt at 137.5°. The crystals are insoluble in ordinary organic solvents, but easily soluble in water, alkali and boiling alcohol.

The chlorplatinate of this substance was prepared and analyzed as follows: A small amount of the compound was dissolved in absolute alcohol and about the calculated quantity of hydrochlorplatinic acid, also in absolute alcohol, was added. Upon the addition of dry benzene, a bright yellow solid separated.

This gave 29.60 per cent. Pt. Calculated for $C_8H_{10}O_6N_4PtCl_6$, 29.71 per cent.

The reaction by which methyl oxalylisourea is formed may be given as follows:

$$CH_3OC(:NH)NH_2 + (COOC_2H_5)_2 \rightarrowtail CH_3OC:N.CO.CONH + 2C_2H_6O$$

Some of the compound, when treated with a little dilute hydrochloric acid, dissolved completely at first and then almost immediately deposited a solid. This solid, dried *in vacuo*, was gently heated, dissolved in alcohol and reprecipitated by petroleum ether. The substance thus obtained began to decompose when heated to 190°. It was undoubtedly oxalylurea.

III. THE AFFINITY CONSTANTS OF ISOUREAS.

For an isourea which is ionized according to

$$HN:C(OR)NH_2,\ H_2O \rightleftarrows HN:C(OR)\overset{+}{N}H_3 + \overline{OH},$$

and which does not belong to the class of strongest bases,[1] such as the alkalies, we would have the affinity constant, K, expressed in the following equation:

$$C_{OH} \times C_P = K \times C_n. \qquad (1)$$

C_{OH} and C_P are the concentrations of the hydroxyl ions and the positive base ions in terms of gram ions per *liter* and C_n is the concentration of the non-ionized amine.

The affinity constants of the most important representatives of the typical classes of isoureas, $H_2NC(OR):NH$, and (alphyl) $HNC(OR):NH$, were determined by the conductivity method as developed by Ostwald,[2] and van't Hoff[3] and as applied especially by Bredig[4] to the measurement of the affinity constants of bases. The proportion (α) of the base ionized in a given solution was ascertained from the molecular conductivity of the solution from the relation

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty} \qquad (2)$$

in which Λ_v expresses the molecular conductivity of the base when 1 gram-molecule is dissolved in v *cc.* water, and Λ_∞ is the extreme molecular conductivity.

[1] For the strongest bases, as is well known, equation (1) does not hold good. Vide Rudolphi: *Ztschr. phys. Chem.*, **17**, 385; Van't Hoff: *Ibid.*, **18**, 301; Kohlrausch: *Ibid.*, **18**, 661. The isomers, as will be shown below, give good constants according to (1) and belong, therefore, to the so-called class of "half electrolytes." (Van't Hoff: "Theoretical and Physical Chemistry," I, p. 117.)

[2] *Ztschr. phys. Chem.*, **2**, 36, 270 (1888).

[3] *Ibid.*, **2**, 781 (1888).

[4] *Ibid.*, **13**, 289 (1893).

Then if we express by Λ the number of liters[1] containing 1 gram-molecule of the amine, equation (1) resolves itself into

$$\frac{\alpha^2}{1-\alpha} = KV. \qquad (3)^2$$

The molecular conductivities Λ_v of the bases were determined by conductivity measurements made with solutions of the free bases. The Kohlrausch apparatus was used and the measurements made at a temperature of 25° (± 0.01°). The molecular conductivities of the bases in the extreme dilution, Λ_∞, were ascertained in the usual way by a determination of the extreme molecular conductivity, Λ'_∞, of the hydrochlorides of the bases—and by calculation of Λ_∞ according to the well-known equation,

$$\Lambda_\infty = \Lambda'_\infty - l_{\infty Cl} + l_{\infty OH} \qquad (4)$$

in which Λ_∞ and Λ'_∞ are the extreme molecular conductivities of the free bases and the hydrochlorides respectively and $l_{\infty OH}$ and $l_{\infty Cl}$ represent the extreme mobility of the hydroxyl and the chlorine ions. $l_{\infty OH}$ was taken as 195.8,[3] $l_{\infty Cl}$ as 75.9,[4] both in reciprocal ohms, for 25°. By combining (2), (3) and (4) the constants, K, were calculated on the basis of the experimental determinations made. The results obtained with the various bases follow:

Methyl Isourea, $HN:C(OCH_3)NH_2$.—Methyl isourea chloride, prepared according to the method of Stieglitz and McKee,[5] and recrystallized twice from boiling absolute methyl alcohol, washed with absolute ether and placed *in vacuo* over solid potassium hydroxide and concentrated sulphuric acid for three days. A solution of some of this salt in water reacted neutral to sensitive litmus paper. An analysis gave 32.22 per cent. Cl. Calculated for $C_2H_6ON_2.HCl$, 32.04.

[1] The conductivity measurements are given in this paper in reciprocal ohms, and all the units used in the measurements are those given in Kohlrausch and Holborn's "Leitvermögen der Elektrolyte," the unit of concentration being the gram-molecule (or equivalent) in 1 cc. The affinity constants, however, are given, in accordance with the more general usage, in terms of the unit of concentration of 1 gram-molecule *per liter*.

[2] Ostwald · *Ztschr. phys. Chem.*, **2**, 278 (1889).

[3] Kohlrausch (*Loc. cit.*, p. 200) gives for $l_{\infty OH}$ at 18° the value 174 in reciprocal ohms. Its value at 25° was calculated with the aid of the temperature coefficient (α) for hydroxyl ions as determined by Loeb and Nernst (*Ztschr. phys. Chem.*, **2**, 963). $\alpha = 0.0159$ and $l_{18} = l_{25}[1 + \alpha(t-25)]$.

[4] Kohlrausch (*Loc. cit.*) gives for the extreme mobility of chlorine ions at 18° the value 65.9. The temperature coefficient for these ions is 0.022 of the value found at 18° (Arrhenius: "Electrochemistry," p. 142).

[5] *Loc. cit.*

The conductivity measurements with this salt are given in Table I, in which v is the volume in liters, containing a gram-molecule of the salt, Λ_v the molecular conductivity at 25° in reciprocal ohms, at the concentration in question. Λ'_∞, the extreme molecular conductivity of the salt, is found according to Ostwald's[1] and Bredig's[2] empirical law from each molecular conductivity, Λ_v, by adding values,[3] d_v, which are characteristic for the differences $\Lambda_\infty - \Lambda_v$, and which are approximately constant for salts in general.

TABLE I.

v.	Λ_v.		Λ'_∞.	
	I.	II.	I.	II.
32	104.06	104.04	119.1	119.0
64	107.97	107.97	119.7	119.7
128	111.30	110.98	119.9	119.6
256	113.15	113.05	119.55	119.7
512	115.87	115.51	120.2	119.8
1024	[120.12]	[118.17]	[123.3]	[121.4]
Means (excluding $v = 1024$):			119.7	119.6

In taking the mean value for Λ'_∞, the value found when $v = 1024$, was excluded because of the obvious fact that at that dilution some irregularity manifests itself. The irregularity is either due to a slight hydrolysis or, much more likely, to the fact that at that dilution methyl isourea begins to act perceptibly as a diacid base.[4]

The agreement between the values for Λ'_∞ in each series and between the means for each series is very satisfactory. This fact shows that, except possibly in very high dilutions (when $v = 1024$) and probably not even then, there is no hydrolysis of the salt of any moment. Even the most dilute solutions were perfectly neutral to sensitive litmus paper and litmus solution.

Since $l_{\infty Cl} = 75.9$ at 25° we have $l_{\infty P} = 119.7 - 75.9 = 43.8$.

[1] "Lehrbuch d. Allgem. Chemie," Vol. II, 693.

[2] *Zischr. phys. Chem.*, **13**, 198.

[3] Bredig's values for dv were used, multiplied by the factor 1.066 to convert the reciprocal Siemens' units into reciprocal ohms (see Kohlrausch: *Loc. cit.*, p. 144, for the use of the factor 1.066 in place of 1.063, the international factor).

[4] Vide, Bredig: *Loc. cit.*, p. 122. For the case in question, the correctness of this latter view is demonstrated by the fact that the weaker bases of the series, the phenylisoureas, do not show any anomaly; their salts would be much more likely to suffer hydrolysis than the salts of the unsubstituted isoureas, but they would be much less likely to behave as diacid bases. Their normal behavior is good evidence, therefore, that the irregularity in the case of methyl and ethyl isourea when v is 1024 is due to the partial ionization of the latter as diacid bases.

That is, the extreme mobility of the positive ion of methyl isourea is 43.8.

The molecular conductivity of the free base in extreme dilution, Λ_∞, is found from equation (4).

$$\Lambda_\infty = l_{\infty P} + l_{\infty OH} = 43.8 + 195.8 = 239.6.$$

A sample of the free base was prepared according to the method of Stieglitz and McKee,[1] and dried next to solid potassium hydroxide for several hours. Its purity was ascertained by titration against tenth-normal hydrochloric acid (with methyl orange as indicator).[2]

0.0939 gram required 12.68 cc. tenth-normal HCl. Calculated, 12.66 cc.

The conductivity measurements for the free base at 25° are given in Table II, in which v and Λv have the same meanings as in Table I. In the third column the values for α are given as calculated according to equation (2), and in the last column the values for the affinity constant, K, are given as determined from equation (3).

TABLE II.

v.	Λv.		100α.		10^5K.	
	I.	II.	I.	II.	I.	II.
32	10.61	10.57	4.43	4.42	6.4	6.4
64	14.60	14.59	6.10	6.10	6.4	6.2
128	20.30	20.22	8.48	8.45	6.1	6.1
256	27.73	27.57	11.55	11.52	5.9	5.9
512	37.93	37.02	15.85	15.47	5.8	5.5
1024	51.74	49.35	21.62	20.62	5.9	5.2
					Means: 6.08	5.90

For comparison, the affinity constant of urea was calculated from the data given by Walker[3] on the hydrolysis of solutions of urea hydrochloride containing varying proportions of the acid and base. The constant, K, was derived according to Walker's formula

$$\frac{\text{Salt}}{\text{Acid} \times \text{Base}} = k$$

in which salt, acid and base represent the concentrations of the substances in gram-molecules per liter. The average constant was found to be 1.28 ($\pm$ 0.06). This constant, according to

[1] *Loc. cit.*

[2] Stieglitz and McKee: *Loc. cit.*

[3] *Ztschr. phys. Chem.*, **4**, 326 (1891) and *Ber. d. chem. Ges.*, **34**, 4117 (1901).

Arrhenius[1] is the constant ratio between the affinity constant of the base and the dissociation constant of water which is 1.2×10^{-14}. We find thus the affinity constant[2] of urea to be $1.28 \times 1.2 \times 10^{-14}$ or 1.54×10^{-14}. Urea is then but little stronger as a base than water—namely, about sixty times as strong.[3] The simplest isourea, methyl isourea, whose affinity constant, as just determined, is 6.4×10^{-5}, is, therefore, 4×10^{9} as strong a base as the parent substance, urea.

It is a base whose affinity is of the order of that of ammonia[4] ($K_{NH_4OH} = 1.8 \times 10^{-5}$).

Guanidine, the amide corresponding to the isourea ethers, is a very much stronger base, standing much closer to the alkalies than to the amines.[5]

Ethyl Isourea, $NH_2C(OC_2H_5):NH$.—Ethyl isourea hydrochloride was recrystallized twice from boiling absolute alcohol. An aqueous solution of the salt was neutral to sensitive litmus paper. The salt was dried for three days over concentrated sulphuric acid and solid potassium hydroxide, and its purity tested by a titration against tenth-normal silver nitrate, which gave 28.61 per cent. Cl. Calculated for $C_3H_8ON_2.HCl$, 28.43 per cent.

The conductivity measurements made with this salt at 25° are given in Table III.

TABLE III.

	Λv.		Λ_∞.	
v.	I.	II.	I.	II.
32	99.10	99.24	114.1	114.2
64	102.72	103.19	114.5	115.0
128	106.59	106.71	115.2	115.3
256	107.60	107.60	114.0	114.0
512	111.20	110.33	115.5	114.6
1024	[114.28]	[114.17]	[117.5]	[117.4]
		Means (excluding $v = 1024$):	114.7	114.6

$$l_{\infty P} = 114.7 - 75.9 = 38.8.$$

The extreme molecular conductivity of the free base Λ_∞ is the sum of 38.8 and 195.8 (the extreme mobility of hydroxl ions), or 234.6.

[1] *Ztschr. phys. Chem.*, **5**, 17 (1892).

[2] Walker (*J. Chem. Soc.* (London) **83**, (1903)), since this was written, has calculated the affinity constant of urea on the basis of a new set of more careful experiments and found $K = 1.5 \times 10^{-14}$. This value is so near the one calculated in the text that we have let the latter stand.

[3] The affinity constant of water, $K = \frac{C_H + C_{OH}}{C_{H_2O}}$ is one fifty-fifth of its dissociation constant, $K = C_H \times C_{OH}$.

[4] Bredig: *Ztschr. phys. Chem.*, **13**, 294, and foot-note p. 293 (1893).

[5] Ostwald: *J. prakt. Chem.*, **33**, 367.

The free base obtained according to the method of Stieglitz and McKee was tested for purity with the following result:

0.0902 gram substance required 10.15 cc. tenth-normal HCl. Calculated, 10.23 cc.

The conductivity measurements and the calculation of the affinity constant, K, follow:

TABLE IV.

	Λv.		100α.		10^5 K.	
v.	I.	II.	I.	II.	I.	II.
8	6.73	6.70	2.87	2.86	10.6	10.5
16	9.58	9.41	4.09	4.02	10.9	10.5
32	13.41	13.18	5.72	5.63	10.9	10.5
64	18.74	18.37	8.00	7.84	10.9	10.4
128	25.91	25.34	11.06	10.80	10.8	10.0
256	35.56	34.30	15.18	14.64	10.6	10.0
					Means: 10.8	10.3

Ethyl isourea is, therefore, nearly twice as strong a base as methyl isourea. It is interesting to observe that the substitution of an ethyl for a methyl group attached to oxygen has caused a much more decided increase in the affinity constant than is the case when a similar single substitution is effected for a methyl group attached to nitrogen (the constants for methyl and ethyl amine are 0.00050 and 0.00056 respectively).

Methyl Phenylisourea, $C_6H_5NHC(OCH_3):NH$.—Pure redistilled methyl phenylisourea was dissolved in absolute ether and a slight excess of dry hydrogen chloride added. The salt was washed with absolute ether and dried *in vacuo* over concentrated sulphuric acid and solid potassium hydroxide for several days. Its water solution was then neutral to sensitive litmus paper. The analysis gave 18.90 per cent. Cl. Calculated, 18.99 per cent.

The conductivity measurements made with this salt at 25° are given in Table V.

TABLE V.

	Λv.			Λ_∞.		
v.	I.	II	III.	I.	II.	III.
32	90.36	90.33	89.79	105.4	105.3	105.8
64	94.49	94.35	94.66	106.3	106.1	106.5
128	96.85	96.85	96.64	105.5	105.4	105.2
256	98.87	98.82	98.79	105.3	105.2	105.2
512	101.07	101.22	100.97	105.4	105.5	105.3
1024	102.55	102.67	102.40	105.7[1]	105.8	105.6
				Means: 105.6	105.6	105.6

$$l_{\infty P} = 105.6 - 75.9 = 29.7.$$

The extreme molecular conductivity of the free base, Λ_∞ is

[1] It is noteworthy, but not unexpected, that in this case there is no abnormal increase of the molecular conductivity (see foot-note p. 459).

the sum of 29.7 and 195.8 (the extreme mobility of hydroxyl ions), or 225.5.

For the measurements of the conductivities of the free methyl phenylisourea, the latter was purified by two redistillations. The base, after it was dried for two days *in vacuo*, gave the following test for purity:

0.2627 gram substance required 17.54 cc. tenth-normal HCl. Calculated, 17.49 cc.

The measurements and the calculation of the affinity constant, K, follow:

TABLE VI.

	$\Lambda v.$		$100\alpha.$		10^5 K.	
$v.$	I.	II.	I.	II.	I.	II.
8	0.307	0.31	0.136	0.138	0.022	0.024
16	0.440	0.445	0.195	0.198	0.024	0.024
32	0.627	0.634	0.278	0.282	0.024	0.025
64	0.909	0.905	0.404	0.402	0.026	0.025
128	1.331	1.331	0.591	0.591	0.027	0.027
256	2.056	2.017	0.913	0.896	0.026	0.032
				Means:	0.025	0.026

The affinity constant of methyl phenylisourea is, therefore, only one-three hundredth that of methyl isourea. It is five hundred times greater than that of aniline[1] ($K = 5 \times 10^{-10}$). The determinations show that it is not sensibly[2] hydrolyzed in dilute solution and the neutrality to sensitive litmus paper and litmus solution confirms this view.

Ethyl Phenylisourea, $C_6H_5NHC(OC_2H_5):NH$.—Ethyl phenylisourea hydrochloride was prepared in exactly the same way as the methyl derivative. A water solution of the salt was neutral to sensitive litmus and a chlorine determination gave 17.76 per cent. Cl. Calculated, 17.57 per cent.

Table VII gives the conductivity measurements made with the salt at 25°.

TABLE VII.

	$\Lambda v.$		Λ_∞.	
$v.$	I.	II.	I.	II.
32	88.70	89.38	103.7	104.4
64	92.86	92.86	104.8	104.7
128	95.90	95.90	104.5	104.5
256	97.51	97.51	103.9	103.9
512	99.67	100.15	104.0	104.4
1024	101.43	101.44	104.6	104.6
			Means: 104.1	104.6

$$l_{\infty P} = 104.3 - 75.9 = 28.4.$$

[1] Bredig: *Loc. cit.*, p. 322.

[2] Within the limits of the sensitiveness of the measurements.

The extreme molecular conductivity of the free base, Λ_∞, is the sum of 28.4 and 195.8 (the extreme mobility of hydroxyl ions), or 224.2.

Ethyl phenylisourea was prepared, purified, and tested for purity exactly as the methyl derivative.

0.4806 gram substance required 29.30 cc. tenth-normal HCl. Calculated, 29.27 cc.

The measurements and the calculation of the affinity constant, K, follow:

TABLE VIII.

	Λv.		100α.		10^5 K.	
v.[1]	I.	II.	I.	II.	I.	II.
26.03	0.822	0.822	0.367	0.367	0.052	0.052
52.07	1.118	1.108	0.499	0.498	0.048	0.048
104.13	1.580	1.571	0.705	0.701	0.048	0.048
208.26	2.314	2.285	1.032	1.019	0.052	0.050
416.53	3.469	3.383	1.548	1.510	0.058	0.056
833.06	5.406	5.253	2.412	2.344	....	....
					Mean: 0.051 ;	0.051

Here again the substitution of the ethyl for the methyl group doubles the strength of the base.

For his interest, constant aid and advice, I wish here to express my great sense of obligation and gratitude to Professor Stieglitz.

KENT CHEMICAL LABORATORY,
UNIVERSITY OF CHICAGO.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 92.]

METAMINOBENZONITRILE AND SOME OF ITS DERIVATIVES.[2]

BY MARSTON TAYLOR BOGERT AND HAL TRUEMAN BEANS.[3]

Received February 6, 1904.

A NUMBER of derivatives of orthoaminobenzonitrile and some of the para compound have been prepared but of those of metaminobenzonitrile only the chloride, chlorplatinate, nitrate, sulphate, and picrate are described in the literature.

[1] An error was made in calculating the amount of the base necessary for a N/32 solution. The volumes, v, given are those actually used.

[2] Read before the New York Section of the American Chemical Society, at its meeting November 6, 1903.

[3] From the dissertation submitted by Mr. H. T. Beans in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

The method of obtaining the orthoaminobenzonitrile published by Bogert and Hand[1] having given such satisfactory results in every respect, it seemed probable the meta compound could be as readily prepared by the same method. It was thought the amino group would prove to be as reactive as that in metanitraniline and by entering into the usual aniline reactions would yield a series of nitriles which apparently have not as yet been prepared, though their corresponding acids and amides have been studied by Chancel, Hofmann, Menschutkin, Griess, Schiff, Traube and others.

For the preparation of *m*-nitrobenzonitrile, two methods were used. The first was that described by Bogert and Hand[2] for the preparation of the corresponding ortho compound. Starting with metanitraniline, the amino group was replaced by cyanogen by the Sandmeyer reaction. This method was found to give fairly satisfactory results with the meta compound but the yields were always lower than those obtained with the ortho body, owing to the marked tendency of the metanitrodiazonium chloride to double into a 3-3′-dinitrodiphenyl by loss of nitrogen, similar to the reaction discovered by Niementowski[3] in the preparation of the chloranilines. The metanitraniline seems to be much more favorable to the production of diphenyl derivatives than the ortho compound and no conditions were found under which their formation in considerable quantities could be avoided.

This unavoidable decrease in the yield due to the formation of diphenyl compounds led to experiments on the direct nitration of benzonitrile and a method was finally found, practically that of Schöpff,[4] which gave entirely satisfactory results. For the reduction of the nitronitrile, the method used was that described by Bogert and Hand[5] for the preparation of the orthoaminonitrile. The reducing agent is a solution of stannous chloride in concentrated hydrochloric acid, the hydrochloride of the amino body being thrown out of solution by a large excess of the concentrated acid as recommended by Friedländer.[6] The free base is readily

[1] This Journal, **24**, 1033.
[2] *Loc. cit.*
[3] *Ber. d. chem. Ges.*, **34**, 3325.
[4] *Ibid.*, **18**, 1063.
[5] *Loc. cit.*
[6] *Monatsh. Chem.*, **19**, 627.

obtained from the hydrochloride by dissolving in water, adding dilute alkali in excess and extracting the solution with ether. By this procedure, the *m*-aminobenzonitrile is readily prepared in considerable quantity and the purification of the crude product is very easily accomplished. There is little or no loss by saponification in either the nitration or reduction reactions and both operations are entirely free from the production of tar or troublesome by-products.

m-Aminobenzonitrile reacts with acids, their anhydrides and chlorides and in some cases with their esters to form *m*-cyananilides which are analogous to the nitranilides produced by similar reactions with *m*-nitraniline.

These substances are the hitherto unknown nitriles of previously described acids and in nearly all cases, are easily hydrolyzed by alkaline hydrogen peroxide to the intermediate amides, many of which have not as yet been described.

In general, the derivatives having the structures

$$O=C\begin{matrix}NH.C_6H_4CN\\X\end{matrix} \quad \text{and} \quad \begin{matrix}CO.NHC_6H_4CN\\|\\CO.X\end{matrix},$$

where X may be the group NH_2, NHC_6H_5 or OC_2H_5, undergo a rather interesting decomposition on heating. In cases where the decomposition occurs, two molecules of the unsymmetrical compound react to produce a molecule each of two symmetrical compounds, as for example,

$$\begin{matrix}H_5C_6NH.CO.NHC_6H_4CN\\H_5C_6NH.CO.NHC_6H_4CN\end{matrix} = O:C\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix} + O:C\begin{matrix}NHC_6H_4CN\\NHC_6H_4CN\end{matrix}$$

m-Aminobenzonitrile also reacts with chloral and bromal to produce addition and condensation products similar to those produced from chloral and the nitranilines.

Experimental.

Preparation of Metanitrobenzonitrile.

(*1*) *From Metanitraniline.*—The method used was that described by Bogert and Hand[1] for the preparation of the *o*-nitrobenzonitrile. By making use of a mechanical stirring apparatus, it was found possible to work with half molecular quantities, the details of the operation being as follows:

[1] *Loc. cit.*

To 100 cc. of concentrated hydrochloric acid, are added 69 grams of finely pulverized *m*-nitraniline and a little water and the mixture warmed gently. The warming and addition of the water in small portions are continued until solution is just effected, when the volume is made up to about 1500 cc. and the solution is stirred rapidly until cold. Usually no nitraniline separates but if it does, under these conditions it will be in a finely divided form and will diazotize very readily. When cooled to 20°, a solution of 35 grams of sodium nitrite in 200 cc. of water is allowed to run into the mixture, drop by drop, with constant stirring. About two hours are necessary for the addition of the sodium nitrite solution and the mixture should then be stirred for an hour longer to insure a complete reaction. The diazo compound is added in very small portions and with constant stirring to a cuprous-potassium cyanide solution prepared by dissolving 125 grams of crystallized copper sulphate in 750 cc. of water, adding 140 grams of potassium cyanide in sufficient water, to the hot solution. This cuprous-potassium cyanide solution is kept at a temperature between 90° and 100° during the addition of the diazo mixture. To secure the best results, it is essential to keep the temperature between the limits given and to add the diazo compound in very small portions and with constant agitation of the reaction-mixture. When all has been added, the solution is at once filtered through a hot-water funnel. On cooling, the *m*-nitrobenzonitrile separates from the solution in long, light yellow, feathery needles. The reddish-brown tar, chiefly 3-3′-dinitrodiphenyl, is repeatedly extracted with boiling water until it yields no more of the nitronitrile. The *m*-nitronitrile seems to show little tendency to retain mineral cyanides as is the case with the ortho compound and hence its purification is much simpler, a single recrystallization from dilute acetic acid usually being sufficient to yield a pure product.

The average of the results obtained from several experiments, using the charges given above, was about 40 grams of pure *m*-nitronitrile and about 30 grams of tarry by-products. Since these results are far from being as satisfactory as those obtained with the ortho compound, various modifications as to temperature, proportions and other conditions were tried but the best method seemed to be that given above.

(2) *By Nitration of Benzonitrile.*—Hofmann[1] nitrated benzonitrile by the action of a mixture of concentrated sulphuric acid and fuming nitric acid and obtained *m*-nitrobenzonitrile. He states that it is necessary to work with small quantities of material and to keep the temperature down to avoid the production of large amounts of nitrobenzoic acid.

Schöpff[2] has applied the method of nitrating benzaldehyde to benzonitrile, using a mixture of concentrated sulphuric acid and the calculated amount of potassium nitrate and it was by practically this same method that we were most successful in obtaining large quantities of *m*-nitrobenzonitrile. The method in detail is given as follows:

To 110 grams of pulverized potassium nitrate, are added 300 cc. of concentrated sulphuric acid and the mass well mixed and cooled to 10°. To this mixture are added, drop by drop, and with constant stirring, 100 grams of benzonitrile. During the addition of the nitrile, the temperature must be watched carefully as it is essential that it should not rise above 20°. In order to maintain this condition, the mixture is surrounded with ice-water when necessary. After a time the acid potassium sulphate begins to separate, forming a thick, pasty mass which is difficult to stir and at this point there is a constant tendency for the temperature to rise above 20°, so that ice or even ice and salt are necessary to prevent loss of the product by overheating. The addition of the benzonitrile requires about three hours and the mixture is then allowed to stand in the cold for an hour to insure a complete reaction. The thick, pasty mass is then added gradually and with stirring, to about two liters of water containing cracked ice. On coming into contact with the water, the product solidifies into a yellow mass, which is broken up and stirred well with the cold water. It is filtered with suction and washed several times with cold water. It is then removed from the funnel and the mass broken up with dilute ammonia, filtered and washed. This treatment is continued until the ammoniacal filtrate is only very slightly yellow in color.

About 118 grams of this product are usually obtained. This is recrystallized once or twice from dilute alcohol or dilute acetic acid, when a nearly pure product, melting at 115° to 116°, is ob-

[1] *Loc. cit.*
[2] *Loc. cit.*

tained. By using this method as given, one kilo of benzonitrile yielded 889 grams of pure *m*-nitrobenzonitrile, or about 89 per cent. of the weight of the benzonitrile used.

When perfectly pure, *m*-nitrobenzonitrile forms long, slender, silky needles of a slightly yellowish color, melting at 117°-117.5° (corr.). When heated above its melting-point it readily sublimes in long, fluffy needles which are nearly colorless. It is easily volatile with steam. Cold glacial acetic acid, chloroform, ethyl acetate, acetone and ether dissolve the compound very readily. It is soluble in hot water, slightly in cold, and easily soluble in hot absolute alcohol, methyl alcohol, carbon tetrachloride, benzene and carbon disulphide, and insoluble in petroleum ether.

PREPARATION OF METAMINOBENZONITRILE.

The preparation of the *m*-aminobenzonitrile from the nitro compound is very readily accomplished by the method given by Bogert and Hand[1] for the reduction of the orthonitrobenzonitrile.

The method giving the best results is to dissolve 500 grams of stannous chloride in about 1500 cc. of concentrated hydrochloric acid. To this solution 100 grams of *m*-nitrobenzonitrile are very gradually added in small portions and with stirring. With each addition of the nitro compound, the temperature rises markedly and the rate of addition should be so regulated that the temperature does not exceed 40°. After a time silky white crystals of the double chloride of tin and the aminonitrile begin to separate, sometimes in such quantities as to render stirring the mass impossible. When this occurs, a little water is added and the reaction-mixture is gently heated in a water-bath until solution is effected and after cooling, the addition of the nitronitrile continued. After all has been added, the mixture is carefully heated until all the crystals are dissolved and then allowed to cool to room temperature, being finally cooled for several hours in a freezing mixture of ice and salt. If much water has been added during the reduction, an equal volume of concentrated hydrochloric acid should be added to the cold solution in order to insure a satisfactory precipitation of the chloride, but this will usually be unnecessary. The fine granular crystals of the chloride are filtered off on a porcelain plate and washed with a small quantity of concentrated hydrochloric acid, previously cooled to —10°.

[1] *Loc. cit.*

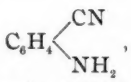
The crystals will still retain a considerable quantity of tin salts, but it is best to wash with only a very small amount of the acid and separate the rest of the tin by other means. Very little of the aminonitrile remains in the mother-liquors and it has not been found practicable to recover this. During the process of reduction there seems to be little or no tendency toward hydrolysis of the nitrile group at temperatures below 40°.

For obtaining the free base from the chloride, either of the following methods may be used.

(1) If the substance is sufficiently free from tin salts, it is convenient to add it in small portions to an excess of dilute ammonia water kept cold by ice. The free base will then separate almost completely in pure white needle crystals.

(2) Since it is very difficult and sometimes impossible to wash out all the tin salts without considerable loss of the amine chloride, it was found best to dissolve it in about 200 cc. of water contained in a liter separatory funnel. A quantity of cracked ice is then added, followed by ether and finally small portions of sodium hydroxide solution until the mixture becomes alkaline. The tin hydroxides at first precipitated will be redissolved and the free aminonitrile is at once taken up by the ether. The alkaline solution is extracted several times with ether, the ethereal solution dried with calcium chloride and the ether then nearly all removed by distillation. The concentrated ethereal solution is then allowed to crystallize, yielding, finally, a solid mass of fine needle crystals. The product thus obtained will usually be very nearly pure. If necessary, however, it may be recrystallized from carbon tetrachloride or gasoline. One crystallization will give a perfectly pure compound. The yield of the aminonitrile as obtained from the ethereal solution averaged from 65 per cent. to 70 per cent. of that theoretically obtainable from the nitronitrile.

m-Aminobenzonitrile,



crystallizes from its ethereal solution in large hexagonal prisms, usually slightly colored. From carbon tetrachloride it is obtained perfectly pure, in long white, silky needles, melting at 53°-53.5° (corr.). It is very soluble in cold chloroform, ethyl acetate, ace-

tone, methyl and ethyl alcohols. It is easily soluble in hot carbon disulphide, carbon tetrachloride, and somewhat soluble in hot water, gasoline and petroleum ether. It distils without decomposition.

Dr. Ferrero, working in this laboratory, attempted the preparation of *m*-aminobenzonitrile by the Griess method,[1] but found it to be quite unsatisfactory. From 20 grams of *m*-uraminobenzoic acid he succeeded in obtaining only 5 grams of very crude aminonitrile, which was difficult to purify. By recrystallization from carbon tetrachloride a fairly pure sample was finally obtained, melting only slightly lower than the product obtained by the other methods, but the process was troublesome and the method was abandoned.

Chloride of m-Aminobenzonitrile,

$$C_6H_4\begin{cases}CN\\NH_2.HCl\end{cases}.$$

—To prepare this salt, *m*-aminobenzonitrile was dissolved in dry ether and to this solution a cold saturated solution of dry hydrochloric acid gas in dry ether was added in excess. The chloride is precipitated in fine, white crystals, from which the excess of acid is removed by careful washing with dry ether. The salt thus prepared forms a mass of silky, white crystals, which, on heating, decompose without melting. It is insoluble in ether, ethyl acetate, benzene, carbon tetrachloride, carbon disulphide and chloroform. Slightly soluble in absolute alcohol and very soluble in water. The salt may be recrystallized from alcohol, forming light, pearly flakes. It is apparently only slightly dissociated by water and is stable in the air, differing markedly in this respect from the ortho compound.

Isophthalonitrile,

$$C_6H_4\begin{cases}CN\\CN\end{cases}.$$

—This compound has been prepared almost entirely from the various sulpho salts by dry distillation methods, but usually in a more or less crude condition, as shown by the melting-points given in the literature.

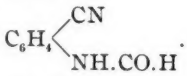
[1] *Ber. d. chem. Ges.*, **8**, 860.

Luckenbach[1] prepared the compound by the removal of hydrogen sulphide from isophthalothiamide, giving the melting-point of the pure substance as 159°-160°. Reinglass[2] obtained the nitrile by dehydrating *m*-cyanbenzaldoxime and gives the melting-point as 157°.

For the preparation of the compound, *m*-aminobenzonitrile was diazotized and the diazo group replaced by the cyanogen group by the Sandmeyer reaction, as described for the preparation of the aminonitrile above. The brownish-yellow reaction-product was dried and extracted with benzene. The crystals obtained from the benzene solution are best purified by dissolving in ethyl acetate and adding gasoline to the hot solution. Thus purified, the isophthalonitrile is obtained as fine, white needles, melting at 161.5°-162° (corr.). It is very soluble in cold chloroform and in hot absolute alcohol, methyl alcohol, benzene, ethyl acetate and ether, and fairly soluble in hot carbon tetrachloride and water. It is insoluble in gasoline, petroleum ether and carbon disulphide.

DERIVATIVES OF METAMINOBENZONITRILE WITH THE FATTY ACIDS.

Formyl-m-aminobenzonitrile,



—Five grams of *m*-aminobenzonitrile were added to about 5 cc. of glacial formic acid. The aminonitrile dissolved with the evolution of considerable heat and the reaction was completed by gently warming for a half hour. On cooling, the reaction-product solidified to a brownish cake, which was broken up with cold water, filtered and washed to remove excess of the acid, and then recrystallized from hot water. The compound crystallizes in white, microscopic needles, which melt at 150.5°-151° (corr.). On adding ammoniacal silver nitrate to its aqueous solution, a white, crystalline precipitate of a silver derivative corresponding to that obtained with formanilide, is at once formed. If this compound is gently heated with water, it dissolves and then deposits metallic silver.

The formyl derivative is soluble in water, chloroform, absolute alcohol, methyl alcohol, and very soluble in ethyl acetate and

[1] *Ber. d. chem. Ges.*, **17**, 1430.
[2] *Ibid*, **24**, 2416.

acetone. It is slightly soluble in hot benzene and ether, and insoluble in carbon tetrachloride, carbon disulphide and petroleum ether.

On analysis, the compound gave 19.25 per cent. N. Calculated, 19.18 per cent.

Acetyl-m-aminobenzonitrile,

—*m*-Aminobenzonitrile dissolves in acetic anhydride with a lowering of the temperature and then after standing a few minutes, the reaction begins with the liberation of considerable heat. The excess of acetic anhydride and acetic acid is very gently boiled off and, on cooling, the brownish oil remaining solidifies. This is dissolved in hot water and allowed to crystallize. Sufficient water must be added to prevent separation as an oil. The acetyl derivative crystallizes in fine, white needles, melting at 130.5°-131° (corr.). It is very easily soluble in cold ethyl acetate, acetone, absolute alcohol, methyl alcohol, chloroform, glacial acetic acid, and in hot water and benzene. It is slightly soluble in hot ether, and insoluble in carbon tetrachloride, carbon disulphide and petroleum ether.

The analysis gave: C, 67.63; H, 4.96; N, 17.50. Calculated: C, 67.50; H, 5.00; N, 17.73.

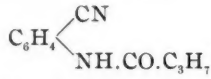
Propionyl-m-aminobenzonitrile,

—For the preparation of this derivative the aminonitrile is dissolved in propionic anhydride. The reaction takes place in much the same way as with the acetyl compound, except that there is apparently no evolution of heat. After warming gently for some time and then carefully distilling off the excess of anhydride and acid, the remaining oil is cooled and dissolved in dilute alcohol, treated with bone-black and allowed to crystallize. The crystals thus obtained are nearly colorless, minute needles. Recrystallized from benzene and a small amount of petroleum ether, the substance is obtained as perfectly white, brilliant needles, melting at 83.5°-84° (corr.).

The propionyl derivative is very easily soluble in cold ethyl acetate, absolute alcohol, methyl alcohol, chloroform, acetone and ether. It is soluble in hot benzene, carbon tetrachloride and carbon disulphide, and slightly soluble in hot water and petroleum ether.

The analysis of the substance gave 16.07 per cent. N. Calculated, 16.09 per cent.

Normalbutyryl-m-aminobenzonitrile,

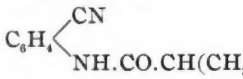


—This derivative was prepared by heating the aminonitrile with an excess of normal butyric anhydride at its boiling-point for an hour. The principal part of the anhydride and acid remaining was removed by careful evaporation and the resulting oil cooled and treated with hot water. On cooling in a freezing-mixture, the oil solidified and was removed from the water and recrystallized from dilute alcohol after treatment with bone-black to remove a slight reddish coloring matter. It was found best to crystallize the material by dissolving in a small amount of alcohol and then adding water till the solution became milky. The solution is then placed in a freezing-mixture and if, on cooling, an oil separates, just sufficient alcohol is added to effect complete solution. From such a solution the butyryl compound separates out almost completely in the form of white, shining flakes. By dissolving in benzene and adding a little petroleum ether, it is obtained in the same form, but the crystals are somewhat larger. The melting-point of the pure substance is 72.5°-73.5° (corr.).

The compound is very soluble in cold ethyl acetate, absolute alcohol, methyl alcohol, chloroform, benzene, ether and acetone. It is soluble in hot carbon tetrachloride, carbon disulphide, and very slightly in hot water. It is insoluble in petroleum ether.

The analysis gave 14.85 per cent. N. Calculated, 14.89 per cent.

Isobutyryl-m-aminobenzonitrile,



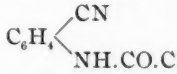
—The isobutyryl derivative was prepared and crystallized in the

same general way as for the normal butyryl compound just described. From dilute alcohol or a mixture of benzene and petroleum ether it is obtained in brilliant, white, pearly flakes, melting at 101° (corr.).

It is very easily soluble in cold ethyl acetate, absolute alcohol, methyl alcohol, chloroform, acetone and ether, and in hot benzene, carbon tetrachloride and carbon disulphide. It is very slightly soluble in hot water and insoluble in petroleum ether.

An analysis of the substance gave 15.23 per cent. N. Calculated, 14.89 per cent.

Isovaleryl-m-aminobenzonitrile,



—This compound was prepared and crystallized in the same way as described for the butyryl derivatives. Considerable difficulty was experienced in obtaining a sharp-melting product, the melting-point rising slightly at each crystallization from dilute alcohol, from 74° up to 77°. Recrystallization of this product from a mixture of benzene and petroleum ether yielded crystals which melted at 77°-78° (corr.), and this melting-point could not be further raised by recrystallization. As obtained in this way, the substance forms nearly white, pearly flakes, which are very easily soluble in cold absolute alcohol, methyl alcohol, ethyl acetate, chloroform and ether. It is easily soluble in hot benzene, carbon tetrachloride and carbon disulphide, and is insoluble in petroleum ether.

A determination of nitrogen gave 13.95 per cent. N. Calculated, 13.86 per cent.

The acyl derivatives of *m*-aminobenzonitrile described are all well defined, crystalline bodies, and are easily obtained in pure condition. It is interesting to note that, with increasing number of carbon atoms in the aliphatic chain, there is a decrease in the melting-point, approaching that of the unsubstituted aminonitrile, and that compounds having the iso structure melt higher than those with normal chains. These facts were also observed with the corresponding compounds of the ortho series and with the quinazolines derived from them. The compounds of the meta series also show an increase in general solubility with increase of

molecular weight. The formyl derivative is soluble in dilute caustic alkali and yields a silver derivative by direct precipitation with ammoniacal silver nitrate, but the other members of the series do not seem to be more soluble in alkali than in water, and do not yield silver salts by direct precipitation. None of the acyl derivatives of this series were found to be volatile with steam, differing in this respect from the ortho compounds.

HYDROLYSIS OF THE NITRILE GROUP.

m-Acetaminobenzamide,

$$C_6H_4\begin{cases}CO.NH_2\\NH.CO.CH_3\end{cases}.$$

—A very convenient and satisfactory method for the hydrolysis of the nitrile group to the corresponding amide was found to be by use of alkaline hydrogen peroxide, as described by Radziszewski.[1] The method was carried out as follows:

Six grams of *m*-acetaminobenzonitrile were heated on the water-bath with about 50 cc. of a 3 per cent. solution of hydrogen peroxide and just sufficient potassium hydroxide to give an alkaline reaction. In about an hour all the crystals had dissolved to a clear, yellowish solution, which was digested for an hour longer, treated with bone-black and allowed to crystallize. The amide crystallizes in fine, white needles, which are purified by recrystallization from hot water. The melting-point of the pure substance was found to be 216°-216.5° (corr.). It is easily soluble in hot water, slightly in cold. It is soluble in hot absolute alcohol and methyl alcohol, very slightly in hot ethyl acetate, carbon tetrachloride, carbon disulphide, chloroform, acetone and benzene, and insoluble in ether and petroleum ether.

DERIVATIVES OF METAMINOBENZONITRILE WITH AROMATIC ACIDS.

For the preparation of the aromatic acid derivatives of *m*-aminobenzonitrile the Schotten-Baumann[2] reaction was used. It was later found that a much more convenient and satisfactory method was to dissolve the aminonitrile in pyridine and add to this solution the calculated amount of the acid chloride or a solution of the latter in pyridine. Under these conditions a complete reaction is secured without the use of alkali. The mixture becomes

[1] *Ber. d. chem. Ges.*, **18**, 355.
[2] *Ibid.*, **19**, 3218.

warm and after the reaction is complete, water is added to take up the excess of pyridine and its hydrochloride. The product is then obtained as an oil, which changes to a crystalline solid on stirring.

Benzoyl-m-aminobenzonitrile,

$$C_6H_4\begin{cases}CN\\NH.CO.C_6H_5\end{cases}.$$

—This compound was prepared by dissolving 3 grams of the aminonitrile in dilute alcohol and adding 5 grams of benzoyl chloride. When the mixture had cooled, a little sodium carbonate solution was added and the mixture warmed on a water-bath. The addition of the carbonate was continued until the solution showed a slight alkaline reaction. On cooling and stirring, the oil solidified to a white, crystalline mass, which was recrystallized from dilute alcohol. The benzoyl derivative separates as pearly flakes which, when pure, melt sharply at 141.5°-142° (corr.). By crystallizing from carbon tetrachloride containing a little ethyl acetate it is obtained in long, glistening needles. It is very easily soluble in cold ethyl acetate, acetone and chloroform, and in hot absolute alcohol, methyl alcohol, benzene and carbon tetrachloride. The compound is slightly soluble in hot water, ether and petroleum ether, and insoluble in carbon disulphide.

An analysis of the substance gave: C, 75.48; H, 4.57; N, 12.85. Calculated: C, 75.67; H, 4.50; N, 12.61.

m-Nitrobenzoyl-m-aminobenzonitrile,

$$C_6H_4\begin{cases}CN\\NH.CO.C_6H_4NO_2\end{cases}.$$

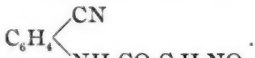
—This compound was prepared by dissolving the aminonitrile in dilute alcohol, adding the calculated amount of finely pulverized *m*-nitrobenzoyl chloride and then sodium carbonate, as in the preparation of the benzoyl derivative. It is much more conveniently prepared by dissolving the nitrile and chloride in separate portions of pyridine, mixing the solutions and precipitating the reaction-product by the addition of water.

By recrystallization from alcohol it is obtained in fine, white needles, which melt at 196.5°-197° (corr.). It is very soluble in cold acetone and ethyl acetate, and in hot absolute alcohol and

methyl alcohol. It is slightly soluble in hot benzene and ether, and insoluble in water, chloroform, carbon tetrachloride, carbon disulphide and petroleum ether.

An analysis of the substance gave 15.63 per cent. N. Calculated, 15.73.

p-Nitrobenzoyl-m-aminobenzonitrile,



—The preparation of this substance was carried out exactly as described for the meta compound. As in the case of the latter, it was found much more convenient to bring about the reaction in pyridine solution.

The para compound is obtained from its solution in boiling alcohol as light yellow needles, which melt at 250°-251° (corr.). It is soluble in hot acetone, absolute alcohol, methyl alcohol, glacial acetic acid, ethyl acetate and isobutyl alcohol. It is insoluble in water, benzene, carbon tetrachloride, carbon disulphide and chloroform.

Benzenesulphone-m-aminobenzonitrile, $C_6H_5SO_2.NHC_6H_4CN$. —For the preparation of this compound 3 grams of the aminonitrile were dissolved in dilute alcohol and 4.5 grams of benzenesulphone chloride added and the mixture warmed with sodium carbonate solution. On cooling, a white, crystalline solid separates, which is best recrystallized from water or dilute alcohol. From the latter solvent it is obtained as long, silky, white needles, melting sharply at 126.5°-127° (corr.). It is soluble in cold ethyl acetate, acetone, ether, absolute alcohol, methyl alcohol and chloroform. It is soluble in hot benzene and water, and insoluble in carbon tetrachloride, carbon disulphide and petroleum ether.

The sulpho compound is easily soluble in cold dilute potassium hydroxide solution or carbonate solution, and is precipitated unchanged by neutralizing with dilute hydrochloric acid. It is also soluble in ammonia water and if silver nitrate solution is added to the ammoniacal solution, a white crystalline precipitate of a silver salt is produced.

A determination of sulphur in the compound gave 12.29 per cent. S. Calculated, 12.40 per cent.

DERIVATIVES OF CARBONIC AND THIOCARBONIC ACIDS.

m-Cyanphenylurethane,

$$C_6H_4\begin{cases}CN\\NH.CO.OC_2H_5\end{cases}.$$

—The acid corresponding to this nitrile has been prepared by Griess[1] and the amide by Wachendorff.[2] The latter was obtained by heating the ethyl ester with aqueous ammonia and is described as crystallizing from benzene in fine needles, melting at 157°-158°.

For the preparation of the nitrile 5 grams of *m*-aminobenzonitrile are dissolved in dilute alcohol and a small amount of sodium carbonate added. To this cold solution are added 5 grams of ethyl chlorcarbonate. The mixture becomes hot and, as the reaction progresses, carbon dioxide is evolved. After a few minutes, more water is added and the mixture warmed on the water-bath. The urethane derivative separates as a dark-colored oil. The reaction mixture is cooled in ice-water and the oil gradually solidifies to a crystalline mass. This is recrystallized from dilute alcohol, best in a refrigerator, since the substance tends to separate as an oil, especially at room temperature. The yield of the pure substance is about 7 grams.

The urethane derivative forms short, prismatic crystals, melting at 61°-62° (corr.), and is very soluble in cold ethyl acetate, ether, benzene, absolute alcohol, methyl alcohol, acetone and chloroform. It is easily soluble in hot carbon disulphide and carbon tetrachloride, and slightly in hot water and petroleum ether.

An analysis of the compound gave 14.83 per cent. N. Calculated, 14.74 per cent.

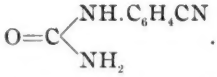
On digesting the urethane derivative with hydrogen peroxide and a little sodium hydroxide the compound melts to an oil and gradually goes into solution, from which *m-urethanebenzamide,*

$$C_6H_4\begin{cases}CO.NH_2\\NH.CO.OC_2H_5\end{cases},$$

crystallizes in fluffy, white flakes, melting at 159°-160°, and corresponding in every way to the compound obtained by Wachendorff.

[1] *Ber. d. chem. Ges.*, **9**, 796.
[2] *Ibid.*, **11**, 701.

m-Cyanphenylurea,



—The acid and the amide corresponding to this nitrile and many derivatives of each have been prepared by Menschutkin[1] and Griess.

For the preparation of the nitrile 3.5 grams of *m*-aminobenzonitrile are dissolved in dry ether and to this solution is added a cold saturated solution of dry hydrochloric acid gas in dry ether. The chloride is at once precipitated as a fine, white, crystalline mass, which is filtered off and washed with ether until free of hydrochloric acid and the ether evaporated in a vacuum desiccator. The chloride is then dissolved in a small amount of water and to this solution is added an aqueous solution of 2.6 grams of potassium cyanate. A white precipitate forms, which redissolves on heating gently on the water-bath. After digesting for an hour, the solution is allowed to cool, causing the separation of a white, flocculent precipitate. When cold, this precipitate changes over into a mass of fine needle crystals, at the same time producing a peculiar crackling sound, sufficiently loud to be heard at a considerable distance. As nearly as could be learned without special study, this sound is produced by a change in crystalline condition. When the compound is crystallized from water solution its melting-point also shows some peculiarities. The compound usually softens very slightly at about 100°, then immediately hardens and melts at about 160°. By recrystallization from a mixture of ethyl acetate and petroleum ether it is obtained in nearly white, microscopic needles, which melt at 160°-162° (corr.).

m-Cyanphenylurea is easily soluble in cold absolute alcohol, methyl alcohol, acetone and ethyl acetate. It is slightly soluble in hot chloroform, and insoluble in petroleum ether, ether, carbon tetrachloride, carbon disulphide and benzene.

A determination of nitrogen gave 25.82 per cent. N. Calculated, 26.08 per cent.

[1] *Ann. Chem.* (Liebig), **153**, 83.
[2] *Ztschr. Chem.*, 1868, 389.

m-Cyancarbanilide,

$$O=C\begin{matrix}NHC_6H_4CN\\NHC_6H_5\end{matrix}$$

—Kühn[1] and Paal[2] have prepared the acid, phenyl-*m*-uramidobenzoic acid, corresponding to this nitrile, but neither the amide nor the nitrile are described in the literature.

For the preparation of the nitrile 5 grams of *m*-aminobenzonitrile are dissolved in dry benzene and to the cold solution 5 grams of phenyl isocyanate are added. The mixture becomes warm and, on cooling, a mass of fine white needles is deposited. This product is recrystallized from alcohol, forming beautiful white needles, which melt at 170.5°-171° (corr.), undergoing decomposition at the same time. The substance is easily soluble in cold absolute alcohol, methyl alcohol, ethyl acetate and acetone. It is slightly soluble in hot water and insoluble in petroleum ether, chloroform, carbon tetrachloride, ether, benzene and carbon disulphide.

A determination of nitrogen in the substance gave 17.61 per cent. N. Calculated, 17.72.

The decomposition of *m*-cyancarbanilide, on heating to its melting-point, seemed to present some interest, and a special study of this reaction was made. When a quantity of material is heated to about 175° in an oil-bath it first melts and then boils with the liberation of phenyl isocyanate, and if the temperature is raised somewhat higher aniline may also be distilled off. Sometimes these vapors reunite in the colder parts of the tube, giving a deposit of carbanilide. There is left behind, after the reaction is completed, a yellowish, glassy mass which, on recrystallization from alcohol, yields white needles, melting at 199°. These were found to be identical in every respect with the di-*m*-cyancarbanilide produced by another method. The decomposition may, therefore, be represented by the following equation:

$$H_5C_6NH.CO.NHC_6H_4CN$$

$$=$$

$$H_5C_6NH.CO.NHC_6H_4CN = O=C\begin{matrix}NHC_6H_4CN\\NHC_6H_4CN\end{matrix} + C_6H_5NH_2 + C_6H_5NCO.$$

[1] *Ber. d. chem. Ges.*, **17**, 2882.
[2] *Ibid.*, **27**, 979.

Di-m-cyancarbanilide,

$$O=C\begin{matrix}NHC_6H_4CN\\NHC_6H_4CN\end{matrix}.$$

—The acid and amide corresponding to this nitrile have been investigated by Griess,[1] Traube,[2] Schiff[3] and others.

In our work it was found possible to obtain the nitrile by a number of reactions.

(1) By heating *m*-cyancarbanilide above its melting-point, as described above.

(2) By heating 1 gram of *m*-aminobenzonitrile and 1.3 grams of *m*-cyanphenylurea to 150°-200° for three hours. Ammonia is liberated during the reaction and there is left a yellowish oil, which solidifies on cooling. This is dissolved in alcohol, treated with bone-black and allowed to crystallize. The crystals thus obtained correspond in every way to those obtained by the other methods, and melt sharply at 199°. The reaction is represented by the equation,

$$O=C\begin{matrix}NHC_6H_4CN\\NH_2\end{matrix}+H_2NC_6H_4CN=O:C\begin{matrix}NHC_6H_4CN\\NHC_6H_4CN\end{matrix}+NH_3.$$

(3) The most direct and convenient method for the preparation of the di-*m*-cyancarbanilide was found to be from phosgen.

To 5 grams of *m*-aminobenzonitrile, dissolved in about 20 cc. of pyridine, were added 10 cc. of a 20 per cent. solution of phosgen in toluene. Considerable heat is liberated in the reaction and after heating for a few minutes, the mixture is cooled and a large volume of water added. As a result, there is obtained a white, crystalline mass which, on recrystallization from dilute alcohol, yields fine, white needles, showing a great tendency to mat down into a compact mass. The product thus obtained melts at 198°-199° (corr.). The substance is easily soluble in cold ethyl acetate, absolute alcohol, methyl alcohol and acetone. It is slightly soluble in hot water and is insoluble in petroleum ether, chloroform, ether, carbon tetrachloride and carbon disulphide.

An analysis of the substance gave 21.42 per cent. N. Calculated, 21.37 per cent.

[1] *Ztschr. Chem.*, 1868, 650.
[2] *Ber. d. chem. Ges.*, **15**, 2128.
[3] *Ann. Chem.* (Liebig), **232**, 140.

m-Cyanthiocarbanilide,

$$S=C\begin{matrix}NHC_6H_4CN\\NHC_6H_5\end{matrix}$$

—The acid corresponding to this nitrile has been prepared and studied by Rathke and Schaefer[1] and Aschan,[2] though there are some wide discrepancies in the results obtained by the two investigators.

Considerable difficulty was experienced in obtaining the nitrile in pure condition, largely due to its great tendency to separate from most solvents either as a thick yellow oil or soft warty masses of crystals. The condensation was brought about in a number of ways: By heating equi-molecular quantities of phenyl mustard oil and *m*-aminobenzonitrile together without a solvent, heating the same in benzene solution, in alcoholic solution and, finally, in an isoamyl alcoholic solution. This last method gave by far the best results and was the one finally adopted.

To a solution of 5 grams of *m*-aminobenzonitrile in 50 cc. of isoamyl alcohol were added 5 grams of phenyl mustard oil and the mixture heated to boiling for about fifteen minutes. The reaction-mixture was allowed to stand in a cold place for some time, when 8 grams of a light yellow, crystalline mass separated out. This was washed free of the amyl alcohol with gasoline, dried on a porous plate, and finally recrystallized by dissolving in hot chloroform and adding petroleum ether until the solution became milky.

The *m*-cyanthiocarbanilide separates from its chloroform solution in light yellow, microscopic, rhombic crystals, melting at 143°-144° (corr.). It is very easily soluble in cold acetone and hot ethyl acetate, absolute alcohol, methyl alcohol and chloroform. It is slightly soluble in hot carbon tetrachloride, ether and carbon disulphide, and insoluble in petroleum ether.

A determination of the sulphur in the compound gave 12.70 per cent. S. Calculated, 12.64 per cent.

Several attempts were made to hydrolyze the nitrile to the corresponding amide, which is not described in the literature, but the compound suffers decomposition on heating with hydrogen peroxide, even in a neutral solution, phenyl mustard oil being liberated.

[1] *Ann. Chem.* (Liebig), **169**, 106.
[2] *Ber. d. chem. Ges.*, **17**, 428.

It was also found impossible to obtain the di-*m*-cyanthiocarbanilide. The usual reaction with carbon disulphide and alkali was tried with negative results. It was then tried to bring about a reaction between *m*-aminobenzonitrile and sodium xanthogenate, but without result. Finally, thiourea and the aminonitrile were heated together, but no product corresponding to the carbanilide could be obtained.

On heating the *m*-cyanthiocarbanilide above its melting-point it undergoes decomposition and pure crystals of thiocarbanilide were obtained, hence the decomposition is probably analogous to that of the *m*-cyancarbanilide described above. It was not found possible, however, to isolate anything from the reaction-product corresponding to the compound sought.

DERIVATIVES OF OXALIC ACID.

Various acids and amides produced by the condensation of *m*-aminobenzoic acid and its amide with oxalic ethyl ester have been prepared and described by Schiff[1] and Griess.[2] Schiff prepares his derivatives by condensation with oxalic ester, while Griess obtained some of the same compound through the hydrolysis of the compound, cyancarbimidaminobenzoic acid, $\begin{matrix}NHC_6H_4CO.OH\\ |\\ CNH\\ |\\ CN\end{matrix}$, which results on passing cyanogen into *m*-aminobenzoic acid. The nitriles, however, are not described in the literature.

Oxal-m-cyananilic Acid Ethyl Ester,

$$\begin{matrix}CO.NHC_6H_4CN\\ |\\ CO.OC_2H_5\end{matrix}$$

—For the preparation of this ester 6 grams of *m*-aminobenzonitrile and 8 grams of ethyl oxalate were heated together for eight hours in a flask surrounded by boiling water. The reaction takes place with the liberation of alcohol and proceeds much more rapidly if the alcohol vapor is removed from the flask, from time to time, by a current of dry air. After from two to three hours' heating the reaction-product begins to separate as a fine crystal-

[1] *Ann. Chem.* (Liebig), **232**, 129.
[2] *Ber. d. chem. Ges.*, **18**, 2410.

line powder, which continues to form until the whole mass becomes solid. At this point the flask is removed and the product washed with cold alcohol to remove the slight excess of oxalic ester and a small amount of a brown coloring-matter formed during the reaction. The fine, white, crystalline mass is then recrystallized from boiling alcohol, yielding usually about 10 grams of the pure product.

Oxal-*m*-cyananilic acid ethyl ester forms short needle crystals of a pure white color, melting sharply at 148°-148.5° (corr.). It is easily soluble in cold acetone, ethyl acetate and chloroform, and in hot absolute alcohol, methyl alcohol and benzene. It is slightly soluble in hot water, carbon tetrachloride, carbon disulphide and ether, and insoluble in petroleum ether.

When heated above its melting-point it undergoes decomposition with the liberation of oxalic ester and formation of oxaldi-*m*-cyananilide, a reaction analogous to the one discovered by Schiff[1] for the corresponding acid. Before this was known, much difficulty was experienced in the preparation of the ester because it was attempted to bring about the condensation by heating the aminonitrile and the oxalic ester at the boiling-point of the latter. Two products were always obtained, the compound sought and the dicyananilide, but the main portion consisted of products which could not be separated. By bringing about the reaction at 100°, as above described, the oxal-*m*-cyananilic ester is the sole product formed.

The analysis of the compound gave: C, 60.69; H, 4.55. Calculated: C, 60.55; H, 4.59.

m-Cyanphenyloxamide,

$$\begin{matrix} CO.NHC_6H_4CN \\ | \\ CO.NH_2 \end{matrix}$$

—The acid and amide corresponding to this nitrile have been prepared by Schiff[1] and Griess.[1]

For the preparation of the compound 2 grams of the oxal-*m* cyananilic ester are heated in a beaker on the water-bath with about 20 cc. of concentrated ammonia solution. The reaction begins in the cold and is completed after a few minutes' heating

[1] *Loc. cit.*

on the water-bath. The heating is continued until the excess of ammonia is removed and the white, silky mass of the amide is then recrystallized from hot alcohol from which it separates in white, pearly flakes. The pure compound melts sharply at 245°-246° (corr.). It is easily soluble in boiling acetone, ethyl acetate, glacial acetic acid, absolute alcohol and methyl alcohol. It is very difficultly soluble in hot water and is insoluble in hot benzene, ether, petroleum ether, chloroform, carbon tetrachloride and carbon disulphide.

When heated above its melting-point it undergoes decomposition analogous to that of the oxal-*m*-cyananilic ester, oxamide subliming into the cool parts of the tube and oxaldi-*m*-cyananilide remaining behind.

An analysis of the *m*-cyanphenyloxamide gave: C, 57.32; H, 3.95. Calculated: C, 57.14; H, 3.70.

Oxal-m-cyananilide,

$$\begin{matrix} CO.NHC_6H_4CN \\ | \\ CO.NHC_6H_5 \end{matrix}$$

—The corresponding acid and amide have been prepared by Schiff[1] by heating the ester with aniline.

On boiling an aniline solution of oxal-*m*-cyananilic ester for a half hour and cooling, a crystalline mass was obtained which consisted mostly of the unchanged ester with a small amount of the *m*-cyananilide sought. Since the reaction takes place so slowly, various condensing agents were tried and of these anhydrous zinc chloride was found to give entirely satisfactory results.

To the aniline solution, as given above, a little anhydrous zinc chloride was added and the mixture boiled for ten minutes, cooled and then alcohol was added. A white, crystalline precipitate separated, which was recrystallized from alcohol.

Prepared in this way, the oxal-*m*-cyananilide forms fine, white, silky needles, which melt at 205°-206° (corr.). It is easily soluble in cold acetone and in hot ethyl acetate, absolute alcohol, methyl alcohol, chloroform and benzene. It is insoluble in petroleum ether, carbon tetrachloride, carbon disulphide, ether and water.

[1] *Loc. cit.*

Oxaldi-m-cyananilide,

$$\begin{matrix} CO.NHC_6H_4CN \\ | \\ CO.NHC_6H_4CN \end{matrix}.$$

—Schiff and Griess have also prepared the acid and amide corresponding to this nitrile.

In this work it was found that a number of reactions would give the dicyananilide, though not all could be used as methods of preparation.

(1) As previously mentioned, when oxal-*m*-cyananilic ester is heated above its melting-point it suffers decomposition. Ethyl oxalate distils off and oxaldi-*m*-cyananilide remains behind as a fine, white, granular mass, hence the reaction probably takes place according to the equation:

$$\begin{matrix} C_2H_5O.OC.CO.NHC_6H_4CN \\ C_2H_5O.OC.CO.NHC_6H_4CN \end{matrix} = \begin{matrix} CO.OC_2H_5 \\ | \\ CO.OC_2H_5 \end{matrix} + \begin{matrix} CO.NHC_6H_4CN \\ | \\ CO.NHC_6H_4CN \end{matrix}.$$

If, however, the heating is not very carefully performed, more deep-seated reactions take place and pure products are not obtained.

(2) On heating *m*-cyanphenyloxamide it decomposes in the same way as the ester above, oxamide subliming into the cold part of the tube and the cyananilide remaining behind as a crystalline powder.

(3) Though the compound sought is formed in each of the above reactions, neither is satisfactory as a method of preparation. It is easily prepared by gently melting equimolecular quantities of oxal-*m*-cyananilic ester and *m*-aminobenzonitrile in the presence of anhydrous zinc chloride. The reaction takes place smoothly and the resulting crystalline mass is recrystallized from hot aniline or amyl alcohol. It is thus obtained as a fine, crystalline powder, which does not melt at 300°, but turns very slightly brown in color. It is soluble in hot glacial acetic acid, aniline and amyl alcohol. It is slightly soluble in hot absolute alcohol, methyl alcohol and acetone, and insoluble in benzene, chloroform, carbon tetrachloride, carbon disulphide, ether, ethyl acetate and petroleum ether.

DERIVATIVES OF SUCCINIC ACID.

Muretow[1] prepared the compound,

$$\begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix} \!\!>\! NC_6H_4CO.OH.$$

which he called succinaminobenzoic acid, by heating *m*-aminobenzoic acid and succinic acid at 200°. By digesting this compound with barium hydroxide solution, he found the imide ring was easily opened with the production of the dicarboxylic acid,

$$\begin{matrix} CH_2CO.NHC_6H_4CO.OH \\ | \\ CH_2CO.OH \end{matrix}$$

Pellizzari[2] obtained the monoethyl ester,

$$\begin{matrix} CH_2CO.NHC_6H_4CO.OH \\ | \\ CH_2CO.OC_2H_5 \end{matrix},$$

of the above acid, by condensing succinic ethyl ester with *m*-aminobenzoic acid. From this ester he obtained the amide and finally the acid which corresponded in every way with the one previously obtained by Muretow. On heating this acid above its melting-point it lost a molecule of water, giving the succin-*m*-aminobenzoic acid of Muretow. As the nitrile and amide derivatives corresponding to these compounds are not described in the literature, it seemed of interest to prepare some of them and study their properties.

Succin-m-cyananilic Acid,

$$\begin{matrix} CH_2CO.NHC_6H_4CN \\ | \\ CH_2CO.OH \end{matrix}.$$

—After numerous attempts it was found impossible to produce the ester of this acid by condensing succinic ethyl ester with *m*-aminobenzonitrile, as Pellizzari had done with *m*-aminobenzoic acid. Even anhydrous zinc chloride failed to bring about the reaction and the method was abandoned.

It was found, however, that quantitative yields of the acid could be readily obtained by the following method, based upon that used by Auwers[3] in the preparation of the succinnitranilic acids.

A boiling, saturated solution of 4 grams (1 mol.) of succinic

[1] *J. Russ. Chem. Soc.*, **4**, 295.
[2] *Gazz. chim. ital.*, **15**, 547.
[3] *Ann. Chem.* (Liebig), **292**, 188.

anhydride in chloroform is prepared, requiring about 200 cc. of chloroform. Benzene may be used in place of the chloroform, but the anhydride is somewhat more soluble in the latter. To this solution is added 4.7 grams (1 mol.) of *m*-aminobenzonitrile in about 50 cc. of chloroform or benzene, and the mixture maintained at the boiling-point of the solvent. Usually after boiling a few minutes the solution will become slightly turbid and then the whole of the reaction-product suddenly crystallizes out of the solution. Sometimes, however, the solution will remain clear, in which case the boiling must be continued until the crystallization occurs. When the reaction is complete the mixture is cooled and filtered, giving a yield of about 7.5 grams of nearly pure succin-*m*-cyananilic acid in the form of fine, glistening needles. An additional small amount of the substance may be obtained from the mother liquor, if desired. The acid is recrystallized from hot water or from a mixture of ethyl acetate and petroleum ether. The following equation represents the formation of the compound:

$$\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array}\!\!>\!O + \begin{array}{l} HNC_6H_4CN \\ | \\ H \end{array} = \begin{array}{l} CH_2CO.HNC_6H_4CN \\ | \\ CH_2CO.OH \end{array}.$$

Succin-*m*-cyananilic acid crystallizes in silky flakes, which melt at 132°-133° (corr.). It is easily soluble in cold ethyl acetate, acetone, absolute alcohol and methyl alcohol. It is slightly soluble in hot chloroform, and is insoluble in ether, carbon disulphide, carbon tetrachloride, petroleum ether and benzene.

Silver Salt of Succin-m-cyananilic Acid,

$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ | \\ CH_2CO.OAg \end{array}.$$

—The silver salt was prepared in the usual way by exactly neutralizing the acid with ammonia and to the hot solution adding silver nitrate solution in slight excess. The salt forms fine, colorless needles, nearly insoluble in cold water, but fairly soluble in hot water. The dry salt is fairly stable in the light.

A determination of the silver content by ignition gave 33.07 per cent. Ag. Calculated, 33.23 per cent.

Calcium Salt of Succin-m-cyananilic Acid,

$$\left(\begin{array}{l} CH_2CO.NHC_6H_4CN \\ | \\ CH_2CO.O. \end{array}\right)_2 Ca.4H_2O.$$

—The calcium salt was formed by adding an excess of pure calcium carbonate to the hot aqueous solution of the acid, filtering and allowing to crystallize. It crystallizes from water in fine, white needles, containing 4 molecules of water of crystallization.

By ignition of the salt to the oxide the following was obtained: 7.31 per cent. Ca. Calculated, 7.35 per cent.

Succin-m-cyananilic Acid Methyl Ester,

$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ | \\ CH_2CO.OCH_3 \end{array}$$

—This ester was prepared by dissolving the acid in absolute methyl alcohol and passing dry gaseous hydrochloric acid into the cold solution until saturated. After cooling, water was cautiously added, care being taken to avoid a rise in temperature before the hydrochloric acid had become diluted. On the addition of the water the ester separates in very fine crystals, which are best recrystallized from dilute methyl alcohol. The pure ester forms long, slender needles, melting at 88°-89° (corr.). It is easily soluble in cold absolute alcohol, methyl alcohol, acetone, ethyl acetate and chloroform. It is easily soluble in hot benzene and carbon tetrachloride, and somewhat soluble in hot ether. The ester is insoluble in petroleum ether and carbon disulphide.

Succin-m-cyananilic Acid Ethyl Ester,

$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ | \\ CH_2CO.OC_2H_5 \end{array}$$

—The ethyl ester was prepared in the same way as the methyl ester, and on the addition of water to its alcoholic solution was obtained in fine, white needles. These may be recrystallized from dilute alcohol or best by dissolving in a very small amount of hot benzene and then adding just sufficient petroleum ether to cause a slight milky appearance. After standing some time, this solution will deposit long, delicate, colorless needles of the pure ethyl ester, melting sharply at 84°-84.5° (corr.). The ester is very easily soluble in cold absolute alcohol, methyl alcohol and chloroform, and in hot benzene, carbon tetrachloride and water. It is insoluble in petroleum ether.

Succin-m-cyananilic Amide,

$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ | \\ CH_2CO.NH_2 \end{array}$$

—The amide may be prepared by treating either the methyl or the ethyl ester with concentrated ammonia water, and boiling gently until all the oily drops have dissolved. The excess of ammonia is then gently evaporated, the solution filtered and allowed to cool. The amide crystallizes from this solution in glistening plates, which are purified by recrystallization from hot water. The pure substance is obtained in fine, white, glistening plates which, if heated quickly, melt rather sharply at 184° (corr.). Immediately upon melting, the mass begins to boil with the evolution of ammonia and the formation of succin-*m*-cyananil. If the melting-point is taken by heating the substance very slowly, according to the usual method, it begins to decompose at a lower temperature and the melting-point is lowered to about 179°-180° (corr.).

The amide is very soluble in hot water and only slightly in cold. It is soluble in hot absolute alcohol, methyl alcohol, acetone and ethyl acetate, and insoluble in petroleum ether, ether, carbon disulphide, carbon tetrachloride, chloroform and benzene.

Succin-m-cyananilic Acid Chloride,

$$\begin{array}{l} CH_2CO.NHC_6H_4CN \\ | \\ CH_2CO.Cl \end{array}$$

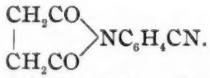
—This chloride is difficult to prepare because of its marked tendency to lose hydrochloric acid and pass into the *m*-cyananil, but after numerous attempts it was finally obtained. To prepare it phosphorus pentachloride and the acid are ground up together and allowed to stand for several hours in the cold, or with only very gentle warming. The mass gradually softens to a pasty consistency and is then extracted with hot chloroform which dissolves the acid chloride. On cooling, the chloroform solution deposits nearly white, shining needles of the chloride, melting sharply at 80° (corr.). At a slightly higher temperature the substance boils with the evolution of hydrochloric acid gas and passes into the *m*-cyananil.

Owing to the difficulties in the preparation of the chloride an analysis was not made, but it was thought that the properties and reactions of the compound were sufficient to identify it as the one sought.

An attempt was made to convert the acid chloride into the methyl ester by dissolving in absolute methyl alcohol. On cooling, fine,

white crystals separated, but these were identified as those of the *m*-cyananil, melting at 137°-137.5° (corr). This reaction illustrates the extreme ease with which hydrochloric acid is liberated from the molecule of the chloride and satisfactorily explains the difficulty of its preparation from the acid.

Succin-m-cyananil,

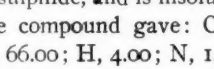


—This compound, the nitrile of the acid prepared by Pellizzari[1] and called by him succinamidobenzoic acid, is obtained, as already described, by the removal of hydrochloric acid from the molecule of the chloride of succin-*m*-cyananilic acid, of ammonia from that of succin-*m*-cyananilic amide and of water from that of succin-*m*-cyananilic acid.

The compound is very easily prepared in pure condition by the latter reaction, especially if a dehydrating agent is used. The best method of procedure is to dissolve the succin-*m*-cyananilic acid in acetic anhydride and distil off the excess of anhydride and acid. A somewhat brownish glass is left, which, on the addition of water, changes to a white crystalline mass. This is dissolved in hot water and allowed to crystallize. The pure anil is thus obtained in brilliant colorless needles, melting sharply at 137°-137.5° (corr.). It is easily soluble in cold chloroform, ethyl acetate and acetone, and in hot benzene, absolute alcohol, methyl alcohol and water. It is slightly soluble in hot ether, carbon tetrachloride and carbon disulphide, and is insoluble in petroleum ether.

The analysis of the compound gave: C, 66.05; H, 4.17; N, 14.08. Calculated: C, 66.00; H, 4.00; N, 14.00.

Succin-m-carbaminanilic Acid,



—One gram of succin-*m*-cyananil was digested at 80°-90° for about one-half hour with 20 cc. of a 3 per cent. solution of hydrogen peroxide and sufficient sodium hydroxide to render the solution slightly alkaline. It was intended to hydrolyze the nitrile group to the amide according to the general reaction. The compound, however, dissolved in the hot solution and, on cooling, no

[1] *Loc. cit.*

crystals were deposited. As it was expected that the amide sought would be quite insoluble in cold water, the solution was examined carefully and found to contain the sodium salt of the succin-*m*-carbaminanilic acid. On acidifying with acetic acid the free acid was obtained in the form of colorless microscopic needles, which melt at 203°-205° (corr.). After a number of trials it was found that hydrogen peroxide alone will not hydrolyze the nitrile group in the *m*-cyananil and the introduction of even a very small amount of alkali causes not only the hydrolysis of the nitrile to the amide, but also the opening up of the imide ring with the formation of an anilic acid derivative, according to the equation:

$$\begin{matrix}CH_2CO\\ |\\ CH_2CO\end{matrix}\!\!>\!NC_6H_4CN + H_2O + NaOH = \begin{matrix}CH_2CO.NHC_6H_4CO.NH\\ |\\ CH_2CO.ONa\end{matrix}.$$

The acid thus produced is soluble in hot water and slightly soluble in hot absolute alcohol, methyl alcohol, ethyl acetate, chloroform, acetone and benzene. It is insoluble in carbon tetrachloride, carbon disulphide, petroleum ether and ether.

Silver Salt of Succin-m-carbaminanilic Acid,

$$\begin{matrix}CH_2CO.NHC_6H_4CO.NH_2\\ |\\ CH_2CO.OAg\end{matrix}.$$

—The silver salt was made in the usual way as described for the silver salt of succin-*m*-cyananilic acid. It precipitates from the hot solution in fine, white, silky crystals, which are not readily changed by the light. The silver content was determined by ignition, which gave 31.45 per cent. Ag. Calculated, 31.45 per cent.

CHLORAL AND BROMAL DERIVATIVES.

Chloral readily forms condensation products with aromatic amines and these products have been the subject of investigation by various workers. Wallach[1] describes the condensation of chloral and aniline with the production of trichlorethylidene-diphenamine, $CCl_3CH\!<\!\begin{matrix}NHC_6H_5\\ NHC_6H_5\end{matrix}$. In 1898 Eibner[2] carefully studied the reaction between aliphatic aldehydes and aromatic

[1] *Ber. d. chem. Ges.*, **5**, 251, and *Ann. Chem.* (Liebig), **173**, 278.
[2] *Ann. Chem.* (Liebig), **302**, 335.

amines and their substitution products and, as a result of his work, was able to state that the true tertiary Schiff bases are not produced with aliphatic aldehydes and aromatic amines, if either are substituted by negative groups. In general, this seems to be true, although Niementowski and Orzechowski[1] describe the derivative of anthranilic acid, $C_6H_4\begin{cases}CO.OH\\N:CHCCl_3\end{cases}$, which is a true Schiff base.

The action of chloral on the nitranilines has been investigated by Eibner,[2] and by Wheeler and Weller.[3] The former obtained, with *p*-nitraniline, two classes of substances, an addition product, $CCl_3CH\begin{cases}OH\\NHC_6H_4NO_2\end{cases}$, and a condensation product, $CCl_3CH\begin{cases}NHC_6H_4NO_2\\NHC_6H_4NO_2\end{cases}$. Wheeler and Weller describe only derivatives of the latter class.

Trichloroxyethylidene-m-cyanphenamine,

$$CCl_3CH\begin{cases}OH\\NHC_6H_4CN\end{cases}.$$

—Anhydrous chloral was prepared by distilling a mixture of chloral hydrate and concentrated sulphuric acid. For the preparation of the addition product 5 grams (1 mol.) of *m*-aminobenzonitrile were dissolved in a mixture of dry gasoline and a small amount of ether. To this solution, cooled in ice-water, were added 6.5 grams (1 mol.) of chloral, diluted with 15 cc. of dry gasoline. The chloral must be added slowly and care taken to avoid a rise in the temperature of the solution. After standing about five minutes, salmon-colored, granular crystals begin to form. The crystallization is complete in a few minutes, and there are usually obtained about 10.5 grams of the reaction-product. This is recrystallized by dissolving in ether and then adding about three volumes of gasoline and evaporating in a current of air dried by sulphuric acid. The addition product, obtained in this way, forms short, prismatic crystals, which melt at 102°-103°

[1] *Ber. d. chem. Ges.*, **28**, 2812.
[2] *Ann. Chem.* (Liebig), **302**, 335.
[3] This Journal, **24**, 1063.

(corr.), decomposing as described below. At 106° the mass becomes solid and remelts at about 165°.

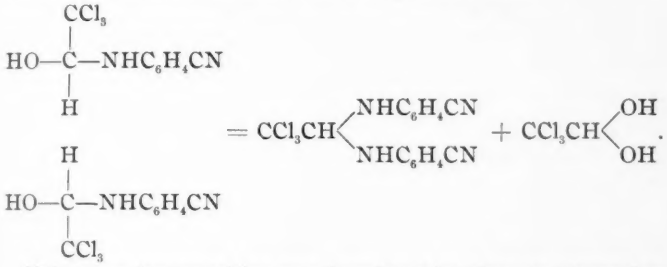
The substance dissolves with decomposition in hot water. It is very soluble in cold absolute alcohol, methyl alcohol, acetone and ether. Less easily in cold benzene, carbon tetrachloride and chloroform, and only slightly soluble in cold petroleum ether.

A determination of chlorine gave 39.69 per cent. Calculated, 40.04 per cent.

It was thought that on heating, the addition product might lose water with the formation of the Schiff base,

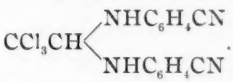
$$CCl_3CH : NC_6H_4CN,$$

but on trying the reaction, chloral and water were liberated and the resulting product was found to be the diphenamine derivative to be described below. Hence the decomposition on heating takes place according to the following equation, and is analogous to that of the *p*-nitraniline derivative, as given by Eibner.[1]



This same decomposition was found to take place on attempting to recrystallize the substance from hot solvents, as for example, boiling carbon tetrachloride. Hence it is essential to proceed according to the method described for the purification of the compound.

Trichlorethylidenedi-m-cyanphenamine,



—This compound results on heating the addition product above its melting-point, as just described, but is best prepared by dissolving 5 grams (2 mol.) of *m*-aminobenzonitrile in about 150 cc. of toluene and adding 3.1 grams (1 mol.) of anhydrous chloral

[1] *Loc. cit.*

in about 50 cc. of toluene. The mixture becomes warm and the flask is at once connected with a return condenser, the contents boiled for a few minutes and then distilled down to small volume. A reddish, granular mass of crystals separates, usually weighing about 6 grams. The reaction product is purified by dissolving in boiling alcohol, treating with bone-black and, after diluting the alcohol with about one-third its volume of water, allowing the solution to crystallize. The pure product thus obtained forms white, needle crystals or sometimes feathery plates, which gradually darken on heating, and melt to a tar at 162°-163° (corr.). If rapidly heated, the gradual charring can be partially prevented and the melting-point is then raised to 165°-167° (corr.). The compound is soluble in cold ethyl acetate and acetone, and in hot chloroform, absolute alcohol, methyl alcohol and benzene. It is insoluble in petroleum ether, water, ether, carbon tetrachloride and carbon disulphide.

It was found possible also to prepare the substance by melting the aminonitrile and chloral hydrate together in the proportion of two molecules of the former to one of the latter. The melt is maintained at a temperature just above 100° for about thirty minutes. On cooling, the reaction product separates, but is usually considerably colored and more difficult to purify than that obtained by the use of anhydrous chloral.

A determination of chlorine gave 29.17 per cent. Cl. Calculated, 29.08 per cent.

Tribromethylidenedi-m-cyanphenamine,

$$CBr_3CH\begin{matrix}NHC_6H_4CN\\ NHC_6H_4CN\end{matrix}.$$

Although the action of chloral on aromatic amines has been the subject of numerous investigations. the action of bromal on the same compounds does not appear to have been tried.

Anhydrous bromal is much more difficult to prepare than the chloral, but after a number of trials it was found that the condensation between the aminonitrile and bromal hydrate could be readily effected if sufficient care as to conditions was observed. This method renders the preparation of the anhydrous bromal unnecessary and greatly simplifies the process.

For the preparation 3 grams (2 mol.) of *m*-aminobenzonitrile

and 3.8 grams (1 mol.) of bromal hydrate are heated together in a flask on a water-bath, which is kept just below the boiling-point. Soon after the substances have melted drops of water begin to separate throughout the mass. From time to time the flask is removed from the heat and the water, which has separated, is removed by drawing a current of dry air through the flask, after which the heating is continued until more water has formed. The reaction is complete when the contents of the flask have changed to a nearly white, granular, crystalline mass. The yield of the product thus obtained is nearly quantitative and if proper precautions have been observed, it is obtained practically pure by digesting a few minutes with petroleum ether to remove the slight excess of aminonitrile. The product is best recrystallized from absolute alcohol, but shows a marked tendency to liberate bromine when heated in any solvent, hence much care is necessary in its purification. If the reaction-product from the condensation is nearly colorless, it is usually better not to attempt to purify it further than with petroleum ether, as given above.

The substance thus prepared does not melt on heating, but suddenly chars to a black tar at about 130°. It is easily soluble in cold acetone, and slightly soluble in hot ethyl acetate, absolute alcohol, methyl alcohol, benzene, chloroform, carbon disulphide and carbon tetrachloride. It is insoluble in petroleum ether and ether.

Wheeler and Gleen[1] have shown that trichlorethylidenedi-*p*-nitrophenamine, on treatment with alcoholic potash, has one chlorine atom replaced by hydroxyl. Since the bromine derivative loses bromine so readily, it was thought that this replacement would occur much more easily than with the chlorine compound. On trying the reaction it was found that a practically quantitative separation of potassium bromide was obtained, but on evaporating the alcoholic solution in a vacuum desiccator only a small amount of a crystalline product was obtained and a brownish oil, having a distinct isonitrile odor, remained. After numerous attempts under various conditions, it was concluded that in the case of this compound the reaction takes a different course, giving a number of by-products, the nature of which has not been discovered.

[1] *J. Elisha Mitchell Sci. Soc.*, **19**, 63.

ACTION OF BROMINE ON *m*-AMINOBENZONITRILE.

Griess[1] treated the aqueous solution of *m*-aminobenzonitrile with bromine water and obtained a precipitate of a bromine substitution product which crystallized from alcohol in white needles. Griess does not describe the compound further.

On adding bromine water to a dilute alcoholic solution of the aminonitrile, a bromine substitution product, identical with the one given by Griess, was obtained, but on repeated crystallization from various solvents it was found impossible to get a product of constant melting-point. The results usually obtained varied from 174° to 178°.

A determination of the bromine in the compound gave 66.86 per cent. Br. Calculated for $C_7H_3N_2Br_3$, 67.60 per cent. Hence the substance is probably a mixture of bromine substitution products, consisting mostly of the tribrom derivative.

On trying the same reaction in glacial acetic acid solution, using a solution of bromine in the same solvent, a product was obtained which showed a higher melting-point, but like the other, was not constant when crystallized from different solvents. However, after repeated crystallizations from alcohol, long, brilliant, colorless needles were obtained, which melted at 177°-178° (uncorr.). This substance, on analysis, was found to be a tribrom substitution product, as shown by the following results: Bromine found, 67.59 per cent. Calculated, 67.60 per cent.

The tribrom-*m*-aminobenzonitrile is easily soluble in cold ethyl acetate and acetone, and in hot absolute alcohol, methyl alcohol, chloroform, carbon tetrachloride and benzene. It is slightly soluble in carbon disulphide and ether, and insoluble in water and petroleum ether.

The bromaminonitrile was saponified by heating 2 grams with 30 cc. of concentrated hydrochloric acid in a sealed tube at 200° for ten hours. On opening the tube a clear solution was obtained which was evaporated to dryness on the water-bath, leaving a white residue almost completely soluble in dilute ammonia. From this solution dilute sulphuric acid precipitates the acid as a fine, white crystalline substance which, on recrystallization from water, gives a product melting rather poorly at 154°-156° (uncorr.). The melting-point of the only tribrom-*m*-aminobenzoic

[2] *Ber. d. chem. Ges.*, 1, 192.

acid, described in the literature, the 2-4-6-tribrom acid[1], is given as 170.5°

As it was found so difficult to obtain sharply melting products by this process of bromination, the work was suspended. It may be possible to obtain bromsubstitution products free of isomers by the method of bromination, so successfully used by Bogert and Hand[2] in their work on the ortho compound, and the matter will be further investigated.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, December, 1903.

ON THE VELOCITIES OF THE IONS IN LIQUID AMMONIA SOLUTIONS.

BY EDWARD C. FRANKLIN AND HAMILTON P. CADY.

Received February 23, 1904.

OBJECT OF THE RESEARCH.

INVESTIGATIONS on the electrical conductivity of liquid ammonia solutions, interpreted in accordance with the theory of electrolytic dissociation, have led to the conclusion that while salts at ordinary dilutions are dissociated to a much greater extent in water than in ammonia, the ions, nevertheless, in the latter solvent, travel with much the greater speed. It was to measure directly the speeds of the ions in liquid ammonia and compare the results thus obtained with the ionic velocities calculated by the method of Kohlrausch from conductivity measurements that this research was undertaken.

HISTORICAL.

Investigations on Liquid Ammonia.—In 1897, Cady[3] made the important discovery that liquid ammonia solutions of certain salts are excellent conductors of electricity, and in explanation of this fact he assumed that ammonia must approximate, or probably even surpass, water in its power to effect electrolytic dissociation.

The same opinion was expressed by Goodwin and Thompson[4] in a paper on the dielectric constant and electrical conductivity of

[1] *Ber. d. chem. Ges.*, **10**, 1708.
[2] This Journal, **25**, 935.
[3] *Jour. Phys. Chem.*, **1**, 707 (1897).
[4] *Phys. Rev.*, **8**, 48 (1899).

liquid ammonia, notwithstanding the fact that they found the dielectric constant of the liquid to be about 22 units,[1] a value which, assuming the approximate validity of the Nerst-Thompson rule places liquid ammonia among the alcohols and far below water in its dissociating power.

It was suggested by Franklin and Kraus, as a result of their investigations on the ebullioscopic behavior of liquid ammonia solutions,[2] that, in all probability, the dissociating power of ammonia is much below that of water, and that the high conductivity of ammonia solutions is rather to be ascribed to the high speed with which the ions travel in this solvent.

In a research on the electrical conductivity of liquid ammonia solutions,[3] the same authors succeeded in establishing a maximum molecular conductivity for a number of salts in liquid ammonia solution, at dilutions very much higher than that required to produce practically complete dissociation in aqueous solutions. It was shown in this investigation, for example, that, whereas in water at 18° the molecular conductivities of the binary alkali metal salts approximate their maximum value of 100 to 130 Kohlrausch units at dilutions of 1,000 to 5,000 liters per molecule, ammonia solutions of the same salts, on the other hand, do not reach their much higher maximum values of 280 to 340 units until the dilution reaches 40,000 to 80,000 liters per gram-molecule. These are facts which, interpreted in accordance with the theory of electrolytic dissociation, lead to the conclusion that the dissociating power of liquid ammonia is comparatively low while the speed with which the ions travel in this solvent is exceptionally high.[4]

It may be worth while to point out here that in further agreement with this conclusion is the fact, frequently observed in this laboratory, that ammonia at —33° is a liquid of much less viscosity than is water at the ordinary temperature.

Measurements of Absolute Ionic Velocities in Aqueous Solutions.—We are indebted to Sir Oliver Lodge[5] for the ingenious conception of actually watching the advance of the ions through

[1] Goodwin and Thompson's measurements were made at —34°. Coolidge (*Wied. Ann.*, **69**, 140 (1899)) obtained 16 as the value of the dielectric constant at 14°.

[2] *Am. Chem. J.*, **20**, 852 (1898), and **21**, 14 (1899).

[3] *Ibid.*, **23**, 297 (1900).

[4] Jones (*Am. Chem. J.*, **25**, 234 (1901)) also points out that it is necessary to assume a high velocity for the ions in liquid ammonia.

[5] British Association Reports, 1886, p. 389.

solutions carrying the electric current. In his experiments on the speed of the hydrogen ions, a glass tube was filled with a jelly made up from agar-agar and a dilute solution of sodium chloride containing a little phenolphthaleïn, and just enough sodium hydróxide to bring out the red color of the dye. The ends of the tube were then inserted in dilute sulphuric acid and a current of electricity was sent from dilute acid to dilute acid through the tube. As the current passed, the progress of the hydrogen ions along the tube was marked by the destruction of the red color of the indicator. His measurements on the speed of the hydrogen ions gave results in fair accordance with the velocity as calculated by the method of Kohlrausch. Similar experiments, however, for obtaining the speeds of other ions gave results differing widely from Kohlrausch's calculated speeds.

W. C. D. Whetham[1] pointed out some of the causes for the discrepancies in Lodge's determinations, improved the method, and obtained values for the speed of a number of ions in water and alcohol solutions which, in some of his measurements, are in good accord with the calculated velocities. The method used will be clear from the following quotation from Whetham's first paper.[2] "Consider the boundary of two solutions of slightly different density, which have one ion in common, but are of different colours. Let us denote the salts by AC and BC. When the current passes across the boundary there will be a transference of C ions in one direction (against the current, if we suppose the C's to be acid radicles, and, therefore, anions), and of A and B ions in the other (in the case supposed, with the current). Since the colour in this case depends on the cation A or B, the boundary will move with the current, and the velocity will indicate that of the ion causing the change in colour." Whetham emphasized the necessity of knowing the electrical potential acting upon the moving ions, and showed how to make a fairly close approximation to a regular fall of potential along the velocity tube, by choosing solutions of nearly equal specific conductivity. He also showed that it is possible to dispense with the jelly in the velocity tube.

Nernst[3] has described a lecture experiment for demonstrating the movement of the permanganate ion against the current in a

[1] *Phil. Trans.*, **184**, 337 (1893), and **186**, 507 (1895).
[2] *Loc. cit.*
[3] *Zischr. Elektrochem.*, **3**, 308 (1896-1897).

solution of potassium permanganate, and at the same time suggests that his method might easily be modified to permit of its use in measuring specific ionic velocities.

Professor Orme Masson[1] has made use of the method of Lodge for the direct measurement of Hittorf's transport numbers. The modifications introduced will be sufficiently obvious from a short description of one of Masson's experiments. Two electrode vessels, containing respectively solutions of copper chloride and potassium chromate, were connected by means of a tube filled with a solution of potassium chloride of known concentration in agar-agar jelly. As the current passes the tube, the yellow and blue boundaries travel to meet each other, and the ratio of the distances traveled in a given time is taken as the ratio of the speeds of the chlorine and potassium ions respectively. Masson showed both experimentally and theoretically that the motion of the boundary, provided the colored ion be chosen specifically slower than the colorless ion, is in reality a measure of the velocity of the latter ion and not that of the colored ion. He showed that under these conditions, the meniscus remains sharp, that there is no mixing of the solutions, and that the concentration of the colorless solution, and with it the slope of potential along this portion of the tube, remains constant independently of the extent of the encroachment of the colored zones.

Since the completion of the work described in this paper, Steele,[2] and Abegg and Gaus[3] have published the results of their important investigations on the velocities of the ions in aqueous solutions.

EXPERIMENTAL.

With the object in view of applying the method worked out by Masson to the measurement of the velocities of the ions in liquid ammonia, we have undertaken the construction of a form of apparatus adapted for use with this volatile liquid. After many changes, including the entire reconstruction of all the essential parts, the apparatus used finally took on the form herewith described.

The Constant Temperature Bath.—The measuring apparatus

[1] *Phil. Trans.*, **192**, 331 (1899).

[2] *Ztschr. phys. Chem.*, **40**, 689 (1902); *J. Chem. Soc.* (London), **79**, 414 (1901); and *Phil. Trans.*, **198**, 105 (1902).

[3] *Ztschr. phys. Chem.*, **40**, 737 (1902).

proper, which includes the test-tube-shaped receptacle *A* (Fig. 2), together with its contents, is kept at a constant temperature by a bath of liquid ammonia contained in the vacuum-jacketed tube *B*.

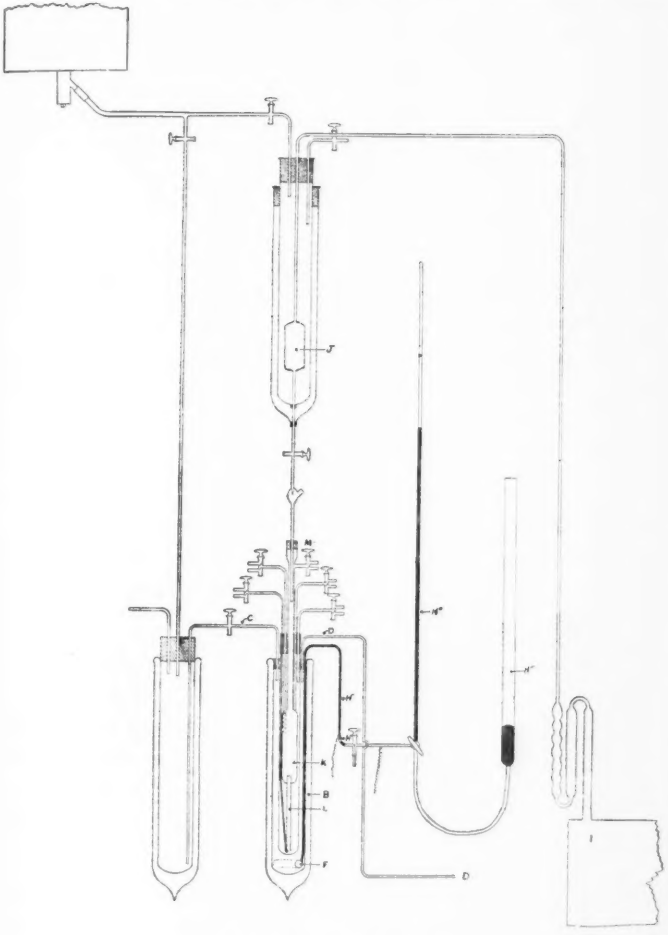


Fig. 1. One-tenth natural size.

Liquid ammonia is supplied to this bath through the tube *C*, while the ammonia gas escapes by way of tube *D*. The temperature of

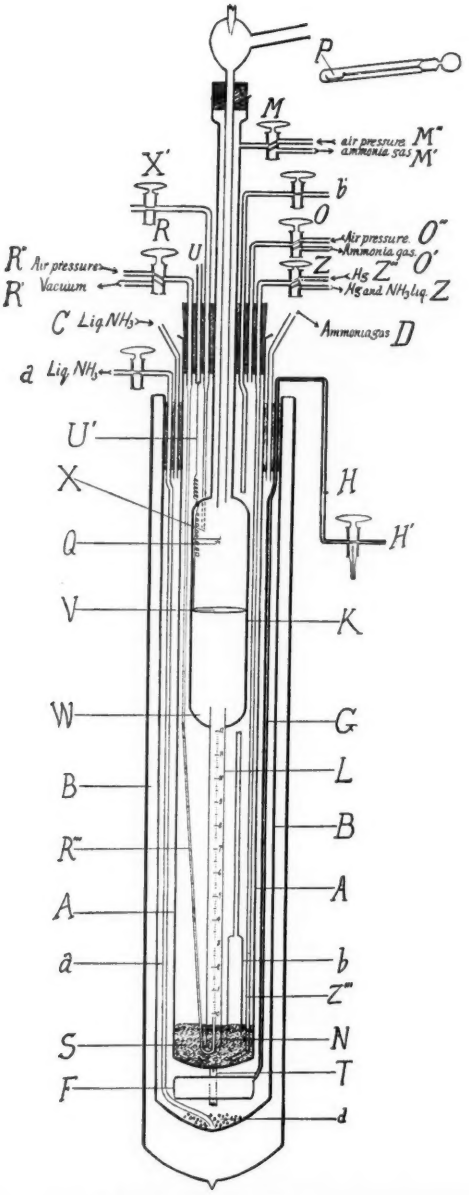


Fig. 2. One-third natural size.

the bath is regulated by an adaptation of Ostwald's constant temperature device. In the figures, *F* and *G H* are the bulb and stem respectively of an air thermometer which is set to maintain the temperature at any constant point by raising or lowering the mercury receptacle *H''*, connected with the stem *H'*, and a barometer tube, *H'''* (Fig. 1). If, after setting the receptacle to correspond to the temperature desired, the temperature of the bath is above that chosen, then the mercury in the thermometer stem fails to make contact at the platinum point *H*, and the passage from *D*, through the proper vessels for protection and capacity, to an ordinary Bunsen vacuum pump, remains unobstructed, with the result that the diminution of pressure on the surface of the liquid brought about by the action of the pump, causes the liquid to boil, and the temperature to fall rapidly. The cooling of the air in the thermometer bulb *F*, soon brings the mercury into contact with the point *H*, thereby completing an electric circuit which includes an ordinary telegraphic relay. This relay in its turn operates a telegraph sounder which is arranged to close down on a piece of rubber tubing inserted in the exit train from *D*, thereby putting the pump out of action. The liquid in the bath then warms up until the contact at *H* is again broken, and the liquid is again set to boiling. This cycle of operations repeats itself every twenty to sixty seconds and maintains the temperature of the bath constant to within 0.2°. To prevent bumping and to insure regular boiling of the ammonia contained in the constant temperature bath a quantity of platinum tetrahedra[1] is placed in the vacuum-jacketed tube at *d*.

The Measuring Cell.—After the constant temperature bath is in operation, ammonia is distilled from the steel cylinder *I* into the receptacle *J* (Fig 1), whence, with the stop-cock *M* (Fig. 2) set to carry off the ammonia gas through *M'*, it is drawn down into the cell *K L*, shown in detail in Fig. 2. Compressed air is then turned on to the surface of the liquid in *K* through the stop-cock *M'' M*. This forces the liquid from the cell *K L*, through the mercury *S*, into the outside compartment *A*, the stop-cock *O* having been previously set to carry off the ammonia gas. These operations are repeated several times until the cell *K L* is thoroughly washed, and the liquid in *A* stands well up on the out-

[1] Beckmann: *Ztschr. phys. Chem.*, **21**, 248 (1896).

side of K. Stop-cock M is then set to open through M' and stop-cock O is turned to admit air pressure to the surface of the liquid in A. This raises a column of mercury in the graduated tube L, and insures against any transfer of material from K to A while the solution is being made up. A weighed quantity of solute is then introduced by means of the platinum spoon at P, and ammonia is run into the cell $K\,L$ in the manner described above until the fine glass pointer Q is covered. Stop-cock O is then turned to shut off the air pressure and to open through O'. This brings the mercury to the same level inside and outside of the tube L. Air pressure is now turned on through $R''R'''$ for the purpose of thoroughly mixing the contents of the cell $K\,L$. After the salt is dissolved and the contents of the cell are homogeneous, R is closed, and air pressure is gradually turned on at stop-cock O. This raises the mercury in the graduated tube L, and the point to which it rises on the scale is read just as the surface of the ammonia in K comes into contact with the pointer Q. This observation, together with the weight of solute introduced, gives the data necessary for calculating the concentration of the solution. With sufficient air pressure through O to maintain a short column of mercury in L, stop-cock R is turned to connect vacuum with the capillary stirring tube R'''. This fills the capillary tube with mercury and thereby precludes any possibility of the solution in L being disturbed by the chance escape of a bubble of air after the meniscus has started up the tube. With stop-cock R closed, and O opened through O', the mercury in the graduated tube L sinks to a level with that outside, while M' and O' opening through short wide tubes into a common receptacle insure against any changes in the level of the mercury at the foot of L during the course of the measurement. The quantity of mercury at S has been previously so fixed as to just cover the end of the capillary tube R''' when the pressure inside and outside the cell $K\,L$ is equalized.

Everything is now ready for beginning the observations on the movement of the meniscus. With the mercury S at the foot of the velocity tube constituting one electrode and the platinum ring V or a ring of mercury in the cup-shaped space W the other, a current of electricity, including in its circuit a rheostat and milliammeter, is turned through the solution in the cell. Connection

is made with the upper electrode through the mercury cup U and the platinum wire U', while the connection from the lower one is through a platinum wire, T, sealed into the bottom of the receptacle A, and thence through mercury contained in a tube sealed over the platinum wire T and reaching the exterior with the other tubes at the mouth of the constant temperature bath. This connection is not shown in the figure. The platinum ring V is used as cathode for the measurement of the ammonium ion, and as anode when observations on the speed of anions are being made. When the speeds of potassium, sodium and silver ions are being measured, the ring of mercury resting in the space W and connected with the ring V is made cathode.

The Cation Boundary.—As the current passes up the tube, mercury ions are formed at the anode, thus giving rise to a solution of mercury salt denser than the solution above it, and serving most excellently the purpose of a cation indicator. With a current of proper strength passing through the tube, the meniscus soon comes out as a very distinct line separating the mercury solution from the superimposed solution. The meniscus is most distinct when observed against a sky background. The position of the meniscus on the scale is read every ten minutes and at the same time a measurement is taken of the current. After the desired number of readings has been made, the contents of the cell $K\,L$ are forced out into the compartment A, and the cell is washed with ammonia after the manner described above, when the cell is ready for beginning another measurement. As the compartment A is filled up past the level X, the excess of ammonia is removed by forcing it out through X', for which purpose the air pressure must be turned on simultaneously through $M''M$ and $O''O$ to avoid disturbing the level of the mercury at the foot of the velocity tube. At the end of a series of measurements the entire contents of A and $K\,L$ are removed through $Z\,Z'$, and the constant temperature bath is emptied through a, air pressure being turned on through $M''M$ and D for this purpose.

The Anion Boundary.—To measure the speed of the anion, an indicator must be introduced into the foot of the velocity tube L, and the direction of the current reversed. Before assembling the apparatus, a quantity of the indicator, compressed into tablets, is packed into the enlarged portion of the tube b, care being taken

to leave a channel for the free passage of air and liquid up the tube. The apparatus is then put together, and mercury is run into the compartment A, through $Z''Z$, until the lower ends of both L and b are well covered. The process of filling the compartment A with ammonia, and the cell $K\,L$ with solution, is then carried out as described above. The level of the liquid in A is adjusted to be somewhat above that of the solution in K, in order that the indicator solution may flow into the foot of the velocity tube as described below. A quantity of lead peroxide is now introduced through the tubulure P, sufficient to cover the surface of the mercury in the bottom of the velocity tube. The lead peroxide is used to prevent the evolution of hydrogen at the cathode and the consequent disturbance to the meniscus by rising bubbles of gas. Mercury is now gradually drawn out of S through the tube Z''' and the stop-cock Z' until the lower end of b is uncovered and ammonia begins to enter the indicator receptacle b. As soon as sufficient solvent has run in upon the indicator to dissolve it, mercury is again run into S to close the mouth of the receptacle b until the indicator is dissolved. The solution of the solid is accompanied by the evolution of heat. To prevent the consequent forcing out of the liquid and the escape of bubbles of air and ammonia gas up through the liquid in compartment A, the stop-cock b' is opened while the indicator is dissolving. The stop-cock b' is now closed, and the mercury in S is again lowered until the dense indicator solution runs out and spreads over the surface of the mercury in the form of a sharply defined layer. The mercury at S is then further carefully lowered until the minute hole N, in the lower end of the graduated tube, is just exposed. The indicator solution flows in quietly and forms a stratum beneath the solution in the velocity tube. As soon as sufficient indicator has entered the tube, mercury is again run into S until the pin-hole N is well covered, when the current is immediately turned on and the observations on the moving meniscus are begun and carried on as described above for the cations. If the operations attendant upon the introduction of the indicator solutions are sucessfully carried out, there is little mixing of the solutions, and the meniscus comes out sharply soon after starting the current. If, however, the solutions are allowed to mix to any considerable extent, a thing which is prevented only by the exer-

cise of the greatest care in manipulation, more time elapses before the meniscus comes out, or it may even fail altogether to appear.

CONDITIONS NECESSARY FOR THE DEVELOPMENT OF A MENISCUS.

From the experimental and theoretical work described in the papers by Whetham,[1] Weber,[2] Kohlrausch,[3] Masson,[4] and Abegg[5] it appears that the conditions affecting the movement of a boundary between two solutions carrying a current are as follows:

(1) *The indicator ion must be specifically slower than the ion whose speed is to be measured.* We have had abundant occasion to confirm this requirement in its application to ammonia solutions. In every case, when a well-formed meniscus is traveling up the velocity tube, separating a faster preceding ion from a specifically slower pursuing one, the reversal of the current soon brings destruction to the meniscus.

Attempts were made to show that the velocity of the meniscus is independent of the indicator ion so long as this fulfils the condition of being specifically slower than the pursued ion. Amalgams of aluminum, lead, bismuth and copper were substituted for pure mercury as anode in a number of experiments. With aluminum no meniscus could be obtained. Bismuth and lead both gave good boundaries, but because of "hydrolysis"[6] of the salts of these metals the results obtained were low. Experiments in which copper and mercury were used to indicate the progress of potassium and ammonium ions show that the speed of the meniscus is, in fact, the same whichever indicator is used.

(2) *If, as in the experiments described in this paper, the meniscus dividing the two solutions travels up the tube, then the indicator solution must be specifically heavier than the superimposed solution.* We learn from the work cited above that the concentration of the indicator solution adjusts itself to that of the solution above in such a way that the concentrations of the two solutions are to each other as the transport numbers of the pursuing and pursued ions. That is, $n/n' = p/p'$, in which n' and p' are the concentration and transference number respectively of the pursuing ion in the indicator solution, and n and p the corre-

[1] *Phil. Trans.*, **184**, 337 (1893), and **186**, 507 (1895).
[2] *Sitzungsber. Akad. Wiss.*, Berlin, 1897, p. 936.
[3] *Wied. Ann.*, **62**, 209 (1897).
[4] *Phil. Trans.*, **192**, 331 (1899).
[5] *Ztschr. Electrochem.*, **7**, 618 (1900-1901).
[6] *Vide*, p. 512.

sponding values for the upper solution. The result of this relation is that the indicator solution will always be the more dilute, a fact which must be taken into consideration in selecting an indicator.

(3) *The current through the tube must not be strong enough to produce a heating effect sufficient to bring about a mixing of the indicator solution into the solution above.* The fact that the specific resistance is greater in the indicator solution determines a greater heating effect in the latter solution. If the difference in the temperature of the two solutions is allowed to become too great, an inevitable mixing of the solutions results. We have frequently observed the destruction of the meniscus from this cause in our experiments. The first indication of danger is the bulging up of the center of the meniscus, to be followed soon by a thin streamer of the indicator solution making its way up through the center of the tube.

A similar relation exists between the resistances of the solution in the velocity tube and in the upper wider portion of the cell. The effect of the greater heating in the narrow tube is to cause a circulation of the solution, which, however, would not be objectionable were it not for the diluting of the solution in the upper portion of the cell by the action of the current at the cathode. The effect of diluting the solution above the meniscus is to produce a sharper fall of potential along the velocity tube and a consequent increase in the speed of the meniscus. This may explain the gradual increase in the velocity of the meniscus observed in the experiments on the potassium, sodium and ammonium ions.

On the other hand, no such acceleration of the motion of the meniscus was observed in the experiments on the speed of the anions. A plausible explanation of this fact is again the action at the upper electrode, which, in these experiments, is made the anode. As is shown (under 4) below, the action of the current at the anode is to increase, or in any event, not to diminish the concentration. A retarding effect, which might be expected as the result of an increase in the concentration of the solution in the velocity tube has, however, not been observed.

(4) *The fall of potential along the tube must be great enough to bring out a sharp meniscus.* In several of our experiments

the difference in density of the solutions used was obviously too slight to permit the realization of this condition. When the attempt was made to use picric acid as indicator for the iodine ion in ammonium iodide and potassium iodide the current could not be made sufficiently strong to bring out a meniscus without at the same time causing much mixing of the solutions. Even with iodoeosine, which seemed to work better than picric acid, mixing still took place to some extent when the current was made sufficiently strong to bring out a good meniscus.

(5) *The action at the electrodes must not be such as to introduce new ions which are faster than the ions traversing the tube.* It is plain that faster ions from either direction entering the velocity tube would alter the potential slope here by an unknown amount and thus render the calculation of the ionic velocities impossible.

That the action at the electrodes produced no disturbing effects in our experiments the following considerations will show. In all measurements on the velocities of the cations the action at the anode consists simply in the formation of the mercury ion, while at the cathode the action depends on the cation undergoing measurement. When this is sodium or potassium, the possible formation of a metalic amide is avoided by using a mercury cathode in which the metal dissolves; when it is ammonium, the action consists in the formation of ammonia and the evolution of hydrogen. When the speed of the anions is being measured, the upper electrode becomes the anode, and, in case the anion is the nitrate ion, the action here consists in the evolution of nitrogen and the formation of ammonium nitrate. This, to be sure, when the salt in the tube is not already ammonium nitrate, introduces a new ion, but in the experiments in which sodium and potassium nitrates are the salts used to furnish the nitrate ions the new ion is not faster than the cation already present. When the halogens are being measured, the action at the anode might be expected to give rise to the formation of halogen substitution products of ammonia, or to the evolution of nitrogen and the formation of ammonium halide, or, as a third possibility, the free halogen itself might be liberated. In our experiments the anode space developed a color as the electrolysis proceeded, which suggested the presence of the

free halogen.[1] At the cathode, on the other hand, while the considerations advanced above show that there is no formation of a new faster ion, there is, especially with ammonium salts, evolution of hydrogen gas which passes up the tube and disturbs the meniscus. This difficulty was overcome by the introduction of a layer of lead peroxide upon the surface of the cathode as depolarizer. The action of the depolarizer in all probability gives rise to the formation of water and a lead salt, or possibly metallic lead, none of which, however, can have any influence upon the motion of the meniscus.

(6) *The salt used for furnishing the indicator ion must be one which does not undergo hydrolysis.*[2]

We have demonstrated in our experiments that this requirement applies also to ammonia solutions. When the attempt was made to use bismuth amalgam for furnishing the indicator ion for an ammonium nitrate solution, it was found that a bulky, white precipitate separated from the bismuth solution and settled on the surface of the bismuth-mercury anode. Lead behaved in a similar manner, but hydrolysis in this case was by no means so marked. Even with mercury, when the iodine ion was present in the standard solution, there was evidence of hydrolytic action. With bromine ions in sodium bromide solution the mercury in-

[1] Moissan (*Compt. Rend.*, **133**, 713 (1901)) states that free chlorine is evolved at the anode when a solution of ammonium chloride in liquid ammonia is electrolyzed at $-35°$.

[2] NOTE.—When the many points of similarity between water and liquid ammonia are recalled, it is not surprising to find that certain salts react with ammonia in a manner entirely analogous to hydrolytic action in aqueous solutions. For example, a reaction parallel to that which takes place when bismuth nitrate is treated with water might be expected to follow the introduction of this salt into liquid ammonia. Bismuth nitrate reacts with water to form basic bismuth nitrate and free nitric acid :

$$Bi(NO_3)_3 + 2H_2O = Bi\begin{<}{OH}{OH}{NO_3}\ + 2HNO_3 = BiONO_3 + 2HNO_3 + H_2O$$

In an analogous manner bismuth nitrate might be expected to react with liquid ammonia to give a compound bearing a relation to ammonia similar to the relation borne by basic bismuth nitrate to water, together with ammonium nitrate, a compound related to ammonia as is nitric acid to water (*Am. Chem. J.*, **23**, 305 (1900)):

$$Bi(NO_3)_3 + 4NH_3 = Bi\begin{<}{NH_2}{NH_2}{NO_3}\ + 2NH_4NO_3 = Bi\begin{<}{NH}{}{NO_3}\ + 2NH_4NO_3 + NH_3$$

That some such action as the one indicated takes place is rendered very probable by the formation of a white mass, soluble in ammonium nitrate, when bismuth nitrate is treated with liquid ammonia, and by the behavior of bismuth and lead solutions described in the paragraph below.

Although it is a rather violent procedure etymologically to use the term hydrolysis in connection with a solvent other than water, we shall nevertheless use the word in this paper with the meaning explained above.

dicator gave an abundant precipitate in the velocity tube; whether, however, the precipitate was the result of hydrolysis or was rather due to the limited solubility of mercury bromide has not been determined. With solutions of nitrates, neither mercury nor copper gave the slightest evidence of hydrolytic action.

Since one of the products of the hydrolysis of salts in ammonia is the formation of ammonium ions, it follows that the indicator solution will contain these faster ions, and that these must interfere with the motion of the meniscus, first, in the case that ammonium ions are in the solution above, by retarding its motion and second, when the pursued ions are potassium or sodium, by destroying the difference of density necessary for the maintenance of a good boundary.

(7) *The fall of potential along that portion of the tube containing the ion whose speed is to be measured must be known.*

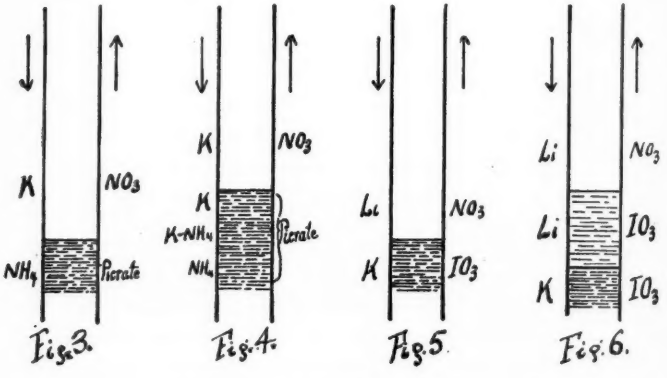
Masson has suggested that this may be accomplished either by measuring the resistance of the upper solution by the method of Kohlrausch, or by direct measurements of the potential slope by means of wires sealed through the walls of the tube. Both methods were tried by us, the latter, in some preliminary experiments on aqueous solutions, without satisfactory results, the former in a modified form of the cell *K L*, with electrodes sealed in for the purpose. Since, however, measurements at the beginning of an experiment, by means of electrodes placed in the upper portion of the cell, could give no certain guarantee that the concentration of the solution in the narrow tube below does not change as it moves up the tube, this device was abandoned, and dependence placed in the theoretical and experimental work referred to above as demonstrating that the concentration of the solution in front of the meniscus and consequently the slope of potential through the tube does not change during the progress of an experiment. The fall of potential along the tube is calculated from the known current and the known constants of the tube and solution in a manner given in detail below.

(8) *The two solutions must contain one ion in common.* We have departed from the conditions laid down by previous investigators in that we have not in all cases used an indicator with one ion in common with the other salt. For example, we have used picric acid, which undoubtedly forms ammonium picrate when it

goes into solution, for indicating the movement of the nitrate ion in potassium nitrate, sodium nitrate and ammonium nitrate, and the concordant results obtained seem to justify the procedure.

A reconsideration of the theory of the moving boundary, moreover, leads to the conclusion that the movement of the boundary must be independent of the nature of both the cation and anion of the indicator so long as the indicator ion itself is specifically slower than the pursued ion.

Consider Figure 3. A solution of sodium nitrate is superim-



posed upon a solution of ammonium picrate. As the current passes down the tube the sodium and ammonium ions travel in the direction of the current, while the nitrate ions move in the opposite direction, followed by the picrate ions. After a short time the condition shown in Fig. 4 is produced; that is, there are now three zones instead of two. Above is the sodium nitrate zone, below which and above the ammonium picrate solution is a layer containing both sodium picrate and ammonium picrate. Since the ammonium ions travel down the tube, none of these can be mixed with the sodium ions at the meniscus and we have thus automatically produced the requirement of Masson that the solutions on each side of the meniscus must contain one ion in common. Even in the case that the upper solution contains the faster potassium ion, the solutions on the two sides of the meniscus will still contain a common ion without any admixture of ammonium ions, for the motion of the latter will always be away from the

meniscus. When the potassium ion follows the ammonium ion down the tube there will be a mixing of the potassium and ammonium picrates in the space below the meniscus. In the case, however, that the cation above is specifically slower than the one below, then a meniscus separating them ought to show itself traveling down the tube. Such a meniscus was observed in the following described experiment. The lower end of the velocity tube was filled with a tenth-normal solution of potassium iodate in 2 per cent. aqueous agar agar jelly upon which an equivalent aqueous solution of lithium nitrate was introduced, as shown in Fig. 5. On passing the current down the tube a very distinct meniscus traveled up the tube from the upper surface of the jelly, marking the progress of the nitrate ions, while at the same time a sharp, but less distinct, meniscus was observed moving from the same starting point down the tube, as shown in Fig. 6.

(9) *Either the indicator or pursued ion must be colored.* We have found that it is not necessary that either solution contain a colored ion for the purpose of making the boundary between the two solutions visible; a slight difference in the refractive index of the two solutions is all that is required.[1]

Following the example of Whetham and of Masson, we considered it necessary in our earlier experiments to introduce a solution of copper into the foot of the graduated tube to form a visible meniscus. This proving itself to be a very troublesome operation, the plan was tried of substituting copper amalgam with bits of amalgamated copper floating on its surface, in place of pure mercury as anode. It was expected that the copper, because of its lower electrolytic solution tension, would go into solution and thus supply the desired colored indicator. However, experiments showed the indicator solution to be a mixture of mercury and copper, the relative quantities of the two metals present depending upon the density of the current. Copper is but slightly soluble in mercury; consequently, when copper amalgam is used as anode the surface layer of the amalgam in contact with the solution is soon so far exhausted of its copper that the potential rises to that required for the solution of the mercury. The result is an indicator solution containing copper and mercury, in some cases, very little copper and much mercury. If the current

[1] Steele (*Phil. Trans.*, **198**, 105 (1902), *J. Chem. Soc.* (London), **79**, 414 (1901), *Ztschr. phys. Chem.*, **40**, 689 (1902)) has antedated us in this discovery.

is weak, or if care is taken to have plenty of copper, better even if some of it is unamalgamated, in the foot of the velocity tube, then the strong blue color of a practically pure copper solution results. In those experiments in which the solution is but slightly colored the meniscus still showed very plainly, an observation which led us to abandon altogether the use of copper and to depend on the mercury alone for supplying the indicator ion.

THE INDICATORS.

The Cathion Indicator.—Mercury, lead, copper and bismuth have been used in the manner described above.

The Anion Indicator.—Since no known material, capable of forming anions under the action of the current, can be used as an electrode after the manner described above for mercury, it is necessary to choose as indicator a salt whose equivalent solution is specifically lighter than the solution to be measured and to introduce it at the top of the graduated tube, or to select one giving an equivalent solution of greater density and place it in the foot of the tube over the mercury cathode. Altogether nine substances were investigated with respect to their behavior as anion indicators, *viz.*, potassium permanganate, ammonium acetate, potassium nitroprusside, potassium argentocyanide, sodium bromate, trinitraniline, picric acid, potassium picrate and iodoeosine. With the exception of sodium bromate, each of these indicators gave a meniscus which could be followed when the current was turned on. Experiments showed that, in all probability, the permanganate ion is faster than the nitrate ion, for the meniscus developed only when the current passed from permanganate to nitrate solution, and faded away when it was reversed. Potassium argentocyanide gave a good meniscus which, however, traveled with, instead of against, the current, as it was expected to do. Among the rest of the indicators picric acid gave the best results in the preliminary test; it was consequently chosen for making most of the measurements given in this paper.

THE MOVING BOUNDARY AND THE ABSOLUTE VELOCITY OF THE IONS.

The experimental and theoretical work cited above[1] show that when a solution containing a salt, AB, is placed in contact with a solution of a second salt, BC, and an electric current is sent

[1] *Vide*, p. 509.

from the one solution to the other, while at the same time the conditions outlined above for the maintenance of a sharp meniscus are realized, then the velocity of the meniscus is identical with the working velocity of the ions *A* and *C*, under the potential gradient realized in the experiment. Consequently

$$U = U_0 \frac{dV}{dl},$$

in which U is the observed velocity of the meniscus, U_0 is the working velocity of the ions under unit potential slope, and dV/dl is the potential slope acting on the ions. No convenient method for measuring dV/dl[1] during the course of an experiment is known, but it may be easily calculated for the solution in front of the meniscus from the known specific resistance of this solution and the cross section of the tube containing the solutions.

From Ohm's law

$$\frac{dV}{dl} = I \frac{dR}{dl}.$$

The work above referred to shows that dV/dl maintains a constant value at the meniscus, therefore

$$U = U_0 I \frac{R_0}{A} \text{ or } U_0 = \frac{UA}{R_0 I},$$

in which I is the current, R_0 is the specific resistance of the solution and A is the cross section of the tube.

But

$$R_0 = \frac{1}{\kappa} = \frac{V}{\Lambda_v}$$

from which it follows that

$$U_0 = U \frac{A\Lambda_v}{IV} \qquad (1)$$

in which κ is the specific conductivity, V is the dilution, and Λ_v is the molecular conductivity of the solution.

This formula permits the calculation of the working velocity of the ion from observations on the speed of the meniscus, U, the cross section of the tube A, the current I, and the values for Λ_v and V from the measurements of Franklin and Kraus.[2]

If the salt is not completely dissociated, and furthermore, if the

[1] *Vide*, p. 513.

[2] *Am. Chem. J.*, **23**, 288 (1900).

assumption is made that the concentration of the solution has no effect on the absolute speeds U_0 of the ions, then

$$U_0 = \frac{U_0}{\alpha} = U \frac{A\Lambda_v \Lambda_\infty}{IV\Lambda_v}$$

or

$$U_0 = \frac{UA\Lambda_\infty}{IV} \qquad (2)$$

CALIBRATION OF THE CELL *K L*.

The tube *L* (Fig. 2) was graduated by the usual method with mercury before it was sealed into the upper portion of the cell. As the mean of four concordant series of measurements it was found that the cross section along the tube is as follows: From 0 to 3 cm., 0.288 sq. cm.; from 3 cm. to 6 cm., 0.287 sq. cm.; from 6 cm. to 9 cm., 0.286 sq. cm.; from 9 cm. to 12 cm., 0.284 sq. cm. The total volume of the cell was determined by weighing the cell empty, and then filling with water from zero on the scale to the glass pointer *Q*, and weighing again. During these operations the lower end of the velocity tube was closed by means of a plug of paraffin. As the mean of four concordant determinations the cell was found to hold 24.49 grams of water at 18°. In calculating the results given in this paper the volume of the cell at the boiling-point of ammonia was assumed to be 24.49 cc. The error thereby introduced is of no significance.

RECORD OF OBSERVATIONS AND CALCULATIONS OF RESULTS.

To show the method of recording the observations and calculating the final results therefrom, a series of measurements on the ammonium ion in a solution of ammonium nitrate, taken from the laboratory note-book, is given in detail.

139.40 milligrams of pure, dry ammonium nitrate, weighed in the platinum spoon *J*, were introduced into the cell *K L* (Fig. 2). After stirring the solution and adjusting the mercury in the velocity tube as described above, the mercury stood at 0.10 cm. on the scale. The volume of the solution was consequently $24.49 - (0.288 \times 0.10) = 24.46$ cc., and the dilution of the solution v was $80 \times 24.46/139.40 = 14.06$. 80 is the molecular weight of ammonium nitrate.

Below is a transcription of the note-book record in which v is

the dilution of the solution, Λ_∞ is the maximum molecular conductivity of ammonium nitrate in Kohlrausch units, taken from the work of Franklin and Kraus, T is the time of making the observations, i is the current in milliamperes measured at time T, I is the mean current for the ten-minute period, S is the position of the meniscus on the graduated tube at time T, 600 u is the distance in centimeters traveled by the meniscus during the ten-minute period, U_0 is the velocity of the ion in centimeters per second per volt calculated by means of the formula (2) above and t is the temperature of the bath.

VELOCITY OF THE CATION IN A SOLUTION OF AMMONIUM NITRATE.

Date: $v = 14.06$. $\Lambda_\infty = 300$. Mercury indicator.

No.	T.	i.	I.	S.	600 u.	U_0.	t.
1	4:15	5.06		1.85			
			4.99		0.65	0.00133	—34.0
2	4:25	4.91		2.50			
			4.83		0.60	0.00127	—34.0
3	4:35	4.75		3.10			
			4.67		0.62	0.00136	—34.2
4	4:45	4.59		3.72			
			4.53		0.59	0.00133	—34.2
5	4:55	4.46		4.31			
			4.40		0.59	0.00137	—34.0
6	5:05	4.33		4.90			
	Current increased.						
7	5:10	5.22		5.20			
			5.12		0.69	0.00136	—34.1
8	5:20	5.02		5.89			
			4.95		0.62	0.00128	—34.2
9	5:30	4.87		6.51			
					Mean:	0.00133	

EXPERIMENTAL RESULTS.

In the following tables the symbols Λ_∞, v, I, 600 u, and U_0 have the significance described above. S' is the point on the velocity tube at which the last reading on the meniscus was taken. Excepting where otherwise indicated, mercury and picric acid were used for cathion and anion indicators respectively. The spaces in the vertical columns indicate points in the progress of the experiments at which the strength of the current was changed.

THE AMMONIUM ION IN A SOLUTION OF AMMONIUM NITRATE.

Λ_∞ FOR $NH_4NO_3 = 300$.

1. $v = 6.28$			2. $v = 14.06$		
I.	600 u.	U_0.	I.	600 u.	U_0.
8.10	0.41	0.00116	4.99	0.65	0.00134
7.91	0.45	0.00130	4.83	0.60	0.00128
7.72	0.43	0.00127	4.67	0.62	0.00136
7.56	0.44	0.00133	4.53	0.59	0.00133
9.48	0.57	0.00138	4.40	0.59	0.00137
9.22	0.50	0.00124	5.12	0.68	0.00136
9.00	0.53	0.00134	4.95	0.62	0.00128
8.77	0.51	0.00133	$S' = 6.50$	Mean :	0.00133
8.56	0.46	0.00122			
8.38	0.52	0.00142			
8.20	0.50	0.00139			
9.60	0.58	0.00138			
9.35	0.54	0.00132			
9.14	0.56	0.00140			
8.95	0.52	0.00133			
8.76	0.53	0.00138			
8.56	0.52	0.00149			
8.38	0.53	0.00144			
$S' = 11.38$	Mean :	0.00133			

3. $v = 58.7$		
2.28	1.26	0.00135
2.14	1.14	0.00131
2.04	1.10	0.00132
1.94	1.06	0.00133
1.84	1.00	0.00133
1.76	0.99	0.00138
1.70	0.95	0.00137
1.64	0.93	0.00139
$S' = 10.63$	Mean :	0.00135

THE AMMONIUM ION IN A SOLUTION OF AMMONIUM IODIDE.

Λ_∞ FOR $NH_4I = 304$.[1]

4.[2] $v = 29.8$		
I.	600 u.	U_0.
4.20	1.10	0.00128
3.75	0.95	0.00124
3.41	0.90	0.00129
3.16	0.80	0.00124
$S' = 5.30$	Mean :	0.00126

5.[3] $v = 31.05$		
I.	600 u.	U_0.
2.51	0.70	0.00131
2.375	0.63	0.00125
2.255	0.62	0.00129
3.19	0.89	0.00131
2.99	0.82	0.00128
2.825	0.79	0.00131
2.685	0.73	0.00127
2.56	0.72	0.00132
2.455	0.70	0.00134
2.37	0.68	0.00134
2.29	0.62	0.00127
$S' = 10.35$	Mean :	0.00130
3.41[4]	1.17	0.00161

[1] Assumed to be the same as ammonium chloride.

[2] In this experiment a precipitate was formed in the indicator solution, probably the result of hydrolysis of the mercury iodide.

[3] Lead amalgam was used as anode in this experiment. The indicator solution here also showed some evidence of hydrolysis, not so marked, however, as in Experiment 4.

[4] The indicator solution was forced out of the velocity tube and the ammonium iodide solution was stirred before making this measurement. In calculating U_0 the dilution of the solution was assumed to remain unchanged.

THE POTASSIUM ION IN A SOLUTION OF POTASSIUM NITRATE.

Λ_∞ FOR $KNO_3 = 338$.

6.

$v = 8.02$

I.	600 u.	U_0.
8.89	0.70	0.00159
8.57	0.75	0.00177
8.30	0.67	0.00163
8.10	0.68	0.00170
7.88	0.70	0.00181
7.69	0.65	0.00171
7.53	0.65	0.00175
7.38	0.65	0.00178
7.21	0.60	0.00168
7.06	0.60	0.00172
6.91	0.65	0.00190
6.78	0.60	0.00179
6.64	0.55	0.00168
$S' = 10.00$	Mean:	0.00174

7.

$v = 9.61$

7.53	0.78	0.00175
7.31	0.74	0.00171
7.09	0.75	0.00179
6.87	0.70	0.00173
6.67	0.72	0.00182
6.49	0.70	0.00182
6.32	0.68	0.00182
6.16	0.65	0.00178
6.02	0.65	0.00182
5.88	0.65	0.00189
5.74	0.65	0.00191
$S' = 9.70$	Mean:	0.00180

8.

$v = 9.62$

8.52	0.85	0.00168
8.16	0.85	0.00178
7.87	0.82	0.00176
7.67	0.79	0.00174
7.44	0.78	0.00177

I.	600 u.	U_0.
9.23	0.95	0.00174
8.86	0.95	0.00182
8.59	0.95	0.00187
8.35	0.93	0.00188
4.28	0.49	0.00194
4.21	0.48	0.00193
$S' = 10.70$	Mean:	0.00181

9.

$v = 23.52$

5.18	1.28	0.00170
4.92	1.15	0.00163[1]
4.68	1.20	0.00177
4.43	1.27	0.00179[2]
4.24	0.98	0.00177[3]
4.07	1.10	0.00186
3.88	1.10	0.00195
3.73	1.00	0.00186
$S' = 11.40$	Mean:	0.00179
7.10	2.25	0.00218[4]

10.

$v = 56.2$

2.58	1.51	0.00170
2.43	1.48	0.00176
2.29	1.35	0.00171
2.16	1.35	0.00181
2.07	1.25	0.00175
2.00	1.25	0.00180
$S' = 10.35$	Mean:	0.00176

11.

$v = 187.5$

1.205	1.15	0.00168
1.16	1.17	0.00178
1.115	1.06	0.00167
1.075	1.12	0.00182
1.025	1.05	0.00179
0.99	1.00	0.00177
$S' = 10.90$	Mean:	0.00176

[1] The current was accidentally interrupted for a short time.

[2] 11 minutes.

[3] 9 minutes.

[4] The liquid in the velocity tube was forced out and this measurement made on the dilute solution from the cathode space. It was assumed in making the calculation that the concentration was unchanged.

THE SODIUM ION IN A SOLUTION OF SODIUM NITRATE.

Λ_∞ FOR $NaNO_3 = 298$.[1]

12.[2]

$v = 4.16$

I.	600 u.	U_0.
9.70	0.37	0.00132
9.59	0.33	0.00120
9.52	0.37	0.00134
9.44	0.33	0.00121
9.36	0.35[3]	0.00124
9.17	0.32[4]	0.00127

$S' = 4.30$ Mean : 0.00126

13[5].

$v = 4.42$

17.44	0.69	0.00129
17.12	0.66	0.00126
16.76	0.64	0.00124
16.44	0.68	0.00134
16.22	0.60	0.00121

$S' = 5.10$ Mean : 0.00127

14.

$v = 9.53$

8.94	0.81	0.00136
8.60	0.74	0.00130
8.29	0.73	0.00133
8.01	0.65	0.00122
7.82	0.67	0.00129
7.61	0.65	0.00129
9.72	0.87	0.00134

$S' = 8.57$ Mean : 0.00132

15.

$v = 11.97$

5.85	0.65	0.00133
5.73	0.60	0.00126
5.60	0.61	0.00131
7.23	0.80	0.00133
6.98	0.75	0.00129
6.80	0.72	0.00127
6.61	0.68	0.00123
9.68	1.15	0.00142
9.33	1.03	0.00133
8.96	1.00	0.00134

$S' = 10.90$ Mean : 0.00131

16.

$v = 35.15$

2.65	0.85	0.00131
3.91	1.23	0.00129
3.72	1.23	0.00136
3.53	1.12	0.00130
3.33	1.10	0.00135
3.22	1.05	0.00134
3.07	1.05	0.00140
2.94	1.00	0.00139

$S' = 10.85$ Mean : 0.00135

17.

$v = 59.8$

2.505	1.33	0.00128
2.345	1.29	0.00133
2.205	1.44[6]	0.00132
2.62	1.51	0.00139
2.45	1.45	0.00143
2.30	1.47	0.00155

$S' = 10.90$ Mean : 0.00138

18.

$v = 62.3$

2.43	1.40	0.00134
2.28	1.32	0.00135
2.15	1.30	0.00144
2.065	1.23	0.00137
1.995	1.20	0.00139
1.91	1.15	0.00139
1.90	1.48[7]	0.00139

$S' = 10.28$ Mean : 0.00138

[1] Assumed 4 units less than sodium bromide.

[2] This experiment was stopped when the meniscus reached 4.30 in the scale, because the current necessary for the production of a good meniscus exceeded the capacity of the milliammeter.

[3] 10.5 minutes.

[4] 9.5 minutes.

[5] A shunt was used in connection with the milliammeter in this experiment. Measurements were interrupted when the meniscus reached 5.10 on the scale by the dropping of crystals of sodium amalgam down the tube from the mercury cathode.

[6] 12 minutes.

[7] 13 minutes.

THE SODIUM ION IN A SOLUTION OF SODIUM BROMATE.

Λ_∞ FOR $NaBrO_3 = 276$.

19.

$v = 33.5$

I.	600 μ.	U_0.
3.51	1.15	0.00129
3.30	1.02	0.00122
3.10	1.03	0.00131
2.92	0.96	0.00130
2.77	0.92	0.00132
2.64	0.90	0.00135
2.54	0.75[1]	0.00137

$S' = 10.08$ Mean : 0.00131

20.

$v = 85.7$

1.26	1.06	0.00130
1.195	1.00	0.00129
1.135	0.95	0.00129
1.07	0.87	0.00126
1.015	0.85	0.00129
0.975	0.82	0.00130
0.935	0.80	0.00132
0.90	0.75	0.00128
0.875	0.76	0.00134

$S' = 9.58$ Mean : 0.00130

1.125	1.20	0.00165[2]
1.055	1.15	0.00169

21.

$v = 109.3$

1.30[3]	0.96[4]	0.00132
1.058	1.23	0.00137[5]
1.025	1.15	0.00135

$S' = 4.10$ Mean : 0.00135

THE SILVER ION IN A SOLUTION OF SILVER NITRATE.

Λ_∞ FOR $AgNO_3 = 295$.[6]

22.

$v = 24.2$

I.	600 μ.	U_0.
3.59	0.68	0.00110
3.61	0.68	0.00109
3.50	0.67	0.00111
3.39	0.63	0.00107
3.32	0.64	0.00112
3.25	0.63	0.00113
3.19	0.62	0.00113
3.27	0.63	0.00112

$S' = 6.95$ Mean : 0.00111

THE NITRATE ION IN A SOLUTION OF AMMONIUM NITRATE.

Λ_∞ FOR $NH_4NO_3 = 300$.

23.

$v = 25.17$

I.	600 μ.	U_0.
3.585	1.00	0.00159
3.535	1.17	0.00187
3.485	1.08	0.00176
3.445	1.09	0.00180
3.385	0.99	0.00167
3.335	1.04	0.00178
3.300	1.02	0.00176

$S' = 10.22$ Mean : 0.00175

[1] 8.5 minutes.

[2] The indicator solution was forced out and readings were begun anew.

[3] 1.30 milliamperes threatened and then destroyed the meniscus.

[4] 5.5 minutes.

[5] The indicator solution was forced out and readings were begun anew. Further measurements were not made for the reason that there was some uncertainty as to the concentration of the solution in the velocity tube.

[6] Unpublished measurements.

THE NITRATE ION IN A SOLUTION OF POTASSIUM NITRATE.

Λ_∞ FOR $KNO_3 = 338$.

24.

$v = 35.6$

I.	600 u.	U_0.
1.05	0.40	0.00174
1.125	0.45	0.00183
1.125	0.45	0.00183
1.115	0.43	0.00176
1.105	0.42	0.00174
1.09	0.43	0.00180
1.315	0.50	0.00174
1.305	0.50	0.00175
1.30	0.52	0.00182
1.675	0.65	0.00178
1.655	0.63	0.00174

$S' = 8.73$ Mean: 0.00178

25.

$v = 94.6$

I.	600 u.	U_0.
0.55	0.57	0.00178
0.55	0.60	0.00188
0.55	0.53	0.00166
0.61	0.62	0.00175
0.608	0.62	0.00176
0.603	0.63	0.00180
0.598	0.60	0.00173
0.645	0.65	0.00174
0.635	0.65	0.00176

$S' = 9.90$ Mean: 0.00176

THE NITRATE ION IN A SOLUTION OF SODIUM NITRATE.

Λ_∞ FOR $NaNO_3 = 298$.[1]

26.

$v = 27.0$

I.	600 u.	U_0.
1.12	0.37	0.00177
1.105	0.36	0.00174
1.09	0.34	0.00167
1.69	0.57	0.00180
1.66	0.55	0.00177
1.625	0.53	0.00174
1.925	0.64	0.00178
1.885	0.65	0.00184
1.85	0.55	0.00159
1.78	0.65	0.00195
1.715	0.57	0.00177
1.70	0.53	0.00167
1.68	0.55	0.00175

$S' = 10.95$ Mean: 0.00175

27.

$v = 28.8$

1.31	0.45	0.00172
1.29	0.45	0.00174
1.55	0.55	0.00178
1.515	0.50	0.00165
1.49	0.53	0.00178
1.785	0.60	0.00169
1.75	0.63	0.00180
1.725	0.60	0.00175
1.70	0.57	0.00168
1.675[2]	0.60	0.00179

$S' = 8.80$ Mean: 0.00174

28.[3]

$v = 35.6$

2.12	0.83	0.00158
2.03	0.87	0.00174
1.95	0.80	0.00166
1.875	0.85	0.00184
1.80	0.70	0.00158
1.73	0.75	0.00180

$S' = 10.00$ Mean: 0.00170

[1] Assumed 4 units less than sodium bromide.

[2] It was attempted at this point to increase the current. 2.3 milliamperes, however, destroyed the meniscus and ended the experiment.

[3] The indicator was considerably mixed with the sodium nitrate solution at the beginning of the experiment. Low results were expected.

THE CHLORINE ION IN A SOLUTION OF AMMONIUM CHLORIDE.

Λ_∞ FOR $NH_4Cl = 304$.

29.

$v = 4.98$

I.	600 u.	U_0.
5.02	0.55	0.00320
4.925	0.55	0.00326
4.925	0.53	0.00316
4.975	0.54	0.00318
5.00	0.46	0.00270
5.00	0.52	0.00302
9.00	1.00	0.00337

$S' = 7.45$ Mean : 0.00309

30.

$v = 8.46$

4.115	0.75	0.00312
4.205	0.70	0.00287
4.255	0.70	0.00284
4.305	0.70	0.00281
4.365	0.70	0.00277
4.425	0.67	0.00262
4.475	0.63	0.00243
4.535	0.70	0.00294

$S' = 10.30$ Mean : 0.00280

31.

$v = 18.23$

3.965	1.23	0.00249[1]
4.415	1.25	0.00227
4.385	1.25	0.00228
4.275	1.15	0.00215
4.09	1.10	0.00216
3.85	1.15	0.00239

$S' = 8.05$ Mean : 0.00229

32.

$v = 40.7$

1.67	1.05	0.00226
2.015	1.27	0.00226
2.085	1.28	0.00220
2.15	1.30	0.00218
2.63	1.55	0.00213
2.705	1.75	0.00231

$S' = 10.40$ Mean : 0.00222

33.

$v = 52.75$

1.38	1.13	0.00227
1.41	1.13	0.00223
1.435	1.14	0.00221
1.46	1.15	0.00218
1.485	1.15	0.00214
1.515	1.15	0.00210
1.54	1.15	0.00208

$S' = 10.50$ Mean : 0.00217

THE CHLORINE ION IN A SOLUTION OF SODIUM CHLORIDE.

Λ_∞ FOR $NaCl = 302$.[2]

34.

$v = 29.45$

I.	600 u.	U_0.
2.15	0.73	0.00168
2.11	0.75	0.00176
2.07	0.75	0.00179
2.025	0.75	0.00183
1.98	0.75	0.00187
1.95	0.70	0.00177
1.92	0.70	0.00180
1.90	0.70	0.00182
1.88	0.70	0.00184
1.845	0.67	0.00180
1.82	0.67	0.00181

$S' = 9.14$ Mean : 0.00180

35.

$v = 58.5$

I.	600 u.	U_0.
1.40	1.03	0.00183
1.385	0.95	0.00170
1.35	0.97	0.00182
1.315	0.97	0.00183
1.285	0.93	0.00178
1.26	0.93	0.00184
1.27	0.92	0.00181
1.28	0.90	0.00176
1.25	0.90	0.00179

$S' = 9.75$ Mean : 0.00180

[1] Bubbles of gas began to appear rising through the velocity tube, the result of omitting inadvertently the lead peroxide. The solution was forced out of the tube, depolarizer was added, and a fresh start made.

NOTE : The anode space was colored yellow, slightly in the dilute solutions, more strongly in the more concentrated.

[2] Assumed same as sodium bromide.

NOTE.—The anode space in both experiments took on a yellow color. The color was stronger in the more concentrated solution.

THE BROMINE ION IN A SOLUTION OF AMMONIUM BROMIDE.

Λ_∞ FOR $NH_4Br = 304$.[1]

36.

$v = 17.01$.

I.	600 u.	U_0.
4.00	0.90	0.00192
3.985	0.93	0.00199
3.975	0.92	0.00198
3.97	0.90	0.00194
3.965	0.92	0.00198
3.97	0.90	0.00194
$S' = 9.47$	Mean :	0.00196

37.

$v = 19.1$

1.97[2]	0.53	0.00205
1.75[2]	0.50	0.00218
1.72[2]	0.40	0.00177
1.72	0.40	0.00177
3.11	0.70	0.00172
3.10	0.80	0.00194
3.095	0.80	0.00197
2.945	0.67	0.00174
2.92	0.78	0.00204
3.75	0.95	0.00193
3.70	0.95	0.00195
$S' = 10.90$	Mean :	0.00188

38.

$v = 41.75$

2.475[3]	1.27	0.00179
2.49	1.35	0.00189
2.495	1.35	0.00188
2.48	1.37	0.00191
2.46	1.32	0.00186
2.40	1.34	0.00194
$S' = 10.53$	Mean :	0.00188
2.47[4]	0.62	0.00176

THE BROMINE ION IN A SOLUTION OF SODIUM BROMIDE.

Λ_∞ FOR $NaBr = 302$.

39.[5]

$v = 21.35$

I.	600 u.	U_0.
2.61	0.65	0.00170
2.135	0.53	0.00169
2.15	0.57	0.00185
2.175	0.55	0.00173
2.15	0.55	0.00174
2.11	0.54	0.00174
2.045	0.53	0.00176
2.00	0.52	0.00177
1.965	0.51	0.00177
1.935	0.52	0.00183
$S' = 8.15$	Mean :	0.00176

40.[6]

$v = 45.7$

1.50	0.82	0.00174
1.375	0.78	0.00185
1.345	0.67	0.00159
1.35	0.72	0.00169
1.295	0.68	0.00167
1.23	0.68	0.00176
1.23	0.62	0.00160
1.215	0.70	0.00183
$S' = 8.10$	Mean :	0.00172

41.

$v = 59.75$

1.015	0.75	0.00179
0.99	0.69	0.00169
0.965	0.70	0.00176
0.935	0.68	0.00177
1.18	0.86	0.00177
1.145	0.84	0.00178
1.120	0.82	0.00178
1.075	0.80	0.00180
1.00	0.78	0.00188
$S' = 9.10$	Mean :	0.00178

[1] Assumed same as ammonium chloride.

[2] These readings were made on the color front, the meniscus not being visible. The succeeding observations were made on the meniscus, which, however, presented a convex front indicative of too strong a current.

[3] This reading was on the color front; those following were made on a very sharp meniscus.

[4] For this measurement the current was reversed. The meniscus gradually faded out. U = 0.62 is for five-minute period.

NOTE.—In these experiments the anode space became colored.

[5] The first four readings were made on the color front, the succeeding ones on a good meniscus.

[6] These measurements were made on a very damp day. Some current leaked through moisture deposited on the stopper, as was proved by testing the apparatus with the cell empty.

NOTE.—The anode space became colored.

THE IODINE ION IN A SOLUTION OF AMMONIUM IODIDE.[1]

Λ_∞ FOR $NH_4I = 304$.[2]

42.

$v = 60.0$

I.	600 u.	U_0.
0.513	0.37	0.00174
0.495	0.38	0.00185
0.743	0.53	0.00172
0.708	0.51	0.00174

I.	600 u.	U_0.
0.685	0.50	0.00176
1.195[3]	0.80	0.00161
1.165[3]	0.73	0.00152
0.625	0.45	0.00173

$S' = 5.90$ Mean : 0.00176

THE IODINE ION IN A SOLUTION OF POTASSIUM IODIDE.[4]

Λ_∞ FOR $KI = 341$.[5]

43.

$v = 57.6$

I.	600 u.	U_0.
0.523	0.27	0.00147
0.510	0.30	0.00166
0.500	0.30	0.00170
0.790	0.45	0.00162

$S' = 2.29$ Mean : 0.00161

44.

$v = 128.0$

I.	600 u.	U_0.
0.450	0.62	0.00176
0.433	0.58	0.00171
0.412	0.50	0.00159
0.725	0.95	0.00161
0.700	0.85	0.00154

$S' = 5.90$ Mean : 0.00164

SUMMARY OF ABSOLUTE VELOCITIES OF THE IONS.

In making up this summary the observations above 6 to 7 on the velocity tube, in the case of the cathions, have been omitted.

The Ammonium Ion of NH_4NO_3.

v.	U_0.
6.28	0.00131
14.06	0.00133
58.5	0.00133

of NH_4I.

v.	U_0.
29.8	0.00126
31.05	0.00129

The Potassium Ion of KNO_3.

v.	U_0.
8.02	0.00172
9.61	0.00178
9.62	0.00177
23.27	0.00174
56.2	0.00175
185.7	0.00171

[1] Several attempts were made to follow the iodine ion in a solution of ammonium iodide by the picric acid ion. A meniscus appeared, but even with the weakest current, which was still strong enough to bring out the meniscus at all, the indicator solution persistently mixed up into the solution above. The difference in the density of the two solutions is probably not sufficiently great. Iodoeosine was used as indicator in this experiment. The dye dissolves readily and forms a solution which is strongly purple when concentrated and yellow when dilute. It gave a very sharp meniscus.

[2] Assumed the same as ammonium chloride.

[3] When the current was increased, the surface of the indicator solution was washed off badly and mixed with the solution above.

[4] Iodoeosine was used as indicator in both these experiments. The meniscus was very sharp, but had the appearance of being washed away from above with the result that the supernatant potassium iodide solution soon became colored. It seems that either the dye contains a faster anion as an impurity, or what is perhaps more likely, the greater heating effect in the dye solution is sufficient to cause the mixing of the slightly denser indicator solution with the solution above. In each experiment, when the current was increased, the meniscus was destroyed.

[5] Assumed the same as KBr.

The Sodium Ion of $NaNO_3$.

v.	U_0.
4.16	0.00126
4.42	0.00127
9.53	0.00130
11.97	0.00130
35.15	0.00132
59.8	0.00131
62.3	0.00132

of $NaBrO_3$.

33.5	0.00129
87.5	0.00129
109.3	0.00135

The Silver Ion of $AgNO_3$.

v.	U_0.
24.2	0.00111

The Nitrate Ion of NH_4NO_3.

v.	U_0.
25.17	0.00175

of KNO_3.

35.6	0.00178
94.6	0.00176

of $NaNO_3$.

27.0	0.00175
28.8	0.00174
35.6	0.00170

The Chlorine Ion of NH_4Cl.

v.	V_0.
4.98	0.00309
8.46	0.00280
18.23	0.00229
40.7	0.00222
52.75	0.00217

of NaCl.

29.45	0.00180
58.5	0.00180

The Bromine Ion of NH_4Br.

v.	V_0.
17.01	0.00196
19.01	0.00188
41.75	0.00188

of NaBr.

21.35	0.00176
45.7	0.00172
59.75	0.00178

The Iodine Ion of NH_4I.

v.	V_0.
60.0	0.00176

of KI.

57.6	0.00161
128.0	0.00164

The results summarized in this table show that the assumption that the speeds of the ions are independent of the degree of dilution is justified in the case of ammonium nitrate, potassium nitrate, sodium chloride and sodium bromide. In solutions of ammonium chloride and ammonium bromide there is obviously a rapid increase in the transport number of the anion with the concentration. Ammonium iodide shows a similar but much less marked behavior.

COMPARISON OF THE OBSERVED IONIC VELOCITIES WITH THE VELOCITIES CALCULATED BY THE METHOD OF KOHLRAUSCH.

Kohlrausch[1] has shown that, for a binary electrolyte, the sum of the speed of the cation and anion traveling under a potential slope 1 volt per centimeter, is

$$U_0+V_0=\frac{\Lambda_\infty}{96540}$$

centimeters per second. In the equation, U_0 and V_0 represent

[1] *Wied. Ann.*, **6**, 196 (1879); Ostwald: "Lehrbuch Allgemeinen Chemie," 2te Aufl., Bd 2, p. 718; Kohlrausch und Holborn: "Leitvermögen der Elektrolyte," p. 105.

the speeds of the cation and anion respectively, and Λ_∞ the maximum molecular conductivity of the salt in Kohlrausch units. By means of this formula, then, the sum of the velocities of the cation and anion of a salt in solution in liquid ammonia may be calculated from the conductivity measurements.

In the table below are given in column 2 the sums of the velocities of the salts indicated in column 1, calculated according to the method of Kohlrausch from the maximum molecular conductivity values of Franklin and Kraus.[1] In columns 3 and 4 are given the directly determined velocities of the cation and anion respectively, in column 5 the sums of these velocities, while in column 6 appears the ratio of Λ_∞ for ammonia solutions at $-33°$ to Λ_∞ for aqueous solutions at $+18°$.

Salt.	$V_\infty/96540$.	U_0.	V_0.	$U_0 + V_0$.	
NH_4NO_3	0.00311	0.00133	0.00176	0.00309	2.4
KNO_3	0.00350	0.00175	0.00176	0.00351	2.7
$NaNO_3$	0.00309	0.00131	0.00176	0.00307	2.8
NaCl	0.00313	0.00131	0.00180	0.00311	2.7
NaBr	0.00313	0.00131	0.00176	0.00307	2.7
$AgNO_3$	0.00306	0.00111	0.00176	0.00287	2.5

TRANSFERENCE NUMBERS IN LIQUID AMMONIA.

The attempt was made to measure the anion transference number for ammonium nitrate and potassium nitrate by observing, after the manner of Masson,[2] the speed with which two boundaries approach each other in the velocity tube. Ammonium acetate was introduced, by a device not shown in the figure, into the space at the top of the tube as anion indicator while the mercury at the bottom of the tube supplied the cation indicator. While in several of the experiments a meniscus was obtained traveling down the tube to meet the boundary from below, in one experiment only, and that the first one upon ammonium nitrate, was the meniscus sufficiently distinct and regular in its motion to permit of readings. In this experiment the boundaries met at 5.90 cm. on the scale, the anion and cation boundaries having traveled respectively 6.00 cm. and 4.35 cm. in two hours. This gives for the ratio, $V/U = 6.00/4.35 = 1.38$, and for the transport number of the anion.

$$V/(U+V) = \frac{6.00}{4.35+6.00} = 0.58.$$

[1] *Am. Chem. J.*, **23**, 277 (1900).
[2] *Phil. Trans.*, **192**, 331 (1899).

The values for the ratio, V_0/U_0, and the transport number, $V_0/(U_0 + V_0)$, for the salts measured calculated from the specific velocities of the ions, are given in the following table :

Salt.	U_0.	V_0.	$\frac{V_0}{U_0}$.	$\frac{V_0}{U_0+V_0}$.	
NH_4NO_3	0.00133	0.00176	1.32	0.570	0.487
KNO_3	0.00175	0.00176	1.00	0.501	0.481
$NaNO_3$	0.00131	0.00176	1.34	0.574	0.577
NaCl	0.00131	0.00180	1.37	0.581	0.596
$AgNO_3$	0.00111	0.00176	1.58	0.614	0.522

In column 6 the transport number of the anion in aqueous solution is given.

The work embodied in this paper was completed in the summer of 1902.

SUMMARY OF RESULTS.

A form of apparatus has been constructed by means of which the absolute velocities of certain ions in liquid ammonia have been determined.

The velocities of a number of univalent ions in liquid ammonia at —33° are from 2.4 to 2.8 times as great as they are in aqueous solutions at 18°, and are in agreement with the velocities calculated from conductivity measurements by the method of Kohlrausch.

LELAND STANFORD JUNIOR UNIVERSITY
AND THE UNIVERSITY OF KANSAS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A RAPID AND CONVENIENT METHOD FOR THE QUANTITATIVE ELECTROLYTIC PRECIPITATION OF COPPER.

BY THEODORE W. RICHARDS AND HAROLD BISBEE.

Received February 23, 1904.

IN ORDER to precipitate copper in a coherent film, suitable for careful washing and accurate weighing, it is necessary that during the electrolytic deposition there should always be enough ionized copper immediately at the surface of the cathode to carry the current from the solution to the electrode. If there is not copper enough present, hydrogen, or some other convenient cation, begins to carry the current, and the film becomes spongy or impure. This case may be discussed as a typical one.

What now are the conditions which determine whether or not enough copper is present to carry the current? Clearly, one of the conditions is the strength of the current to be carried. Corresponding to every solution, other conditions being fixed, is a maximum current which must not be exceeded. The rate of total precipitation is, of course, dependent upon this total current strength. Another is the area of the electrode on which the deposition is to be conducted, for only the copper in the immediate vicinity of the electrode can be deionized, and the greater the area the more copper is available, other conditions being equal. Therefore, the permissible rate of deposition and, consequently, the maximum current strength depends upon the area. Thus, it is the *current density,* or the strength of current for each unit of area, which determines whether or not a given cation is deposited in a pure state, other conditions being equal. Bunsen pointed out this fact many years ago.

Another essential condition which affects the permissible speed of precipitation is obviously the concentration of the solution of copper, for the more concentrated the solution the more copper will be present at the cathode ready for precipitation. Since ionization is an extremely rapid process, the whole of the copper present is probably available as a carrier, not merely that which is ionized. The "associated" portion ionizes at once as soon as the ionized portion is removed.

It is, of course, true that the single potential difference at the cathode, if measurable, would be an approximate index of the nature of the deposit, for this single potential difference rises in a mixture when the current density is increased above the "carrying power" of the most easily deposited ion. But, as is well known, the single potential difference would be at best only an approximate index, since with a single metal it varies over several tenths of a volt with varying concentration. As a matter of fact, the single potential difference at the cathode is not easily found, even arbitrarily, in actual analysis. The total difference of potential between the electrodes (or "Klemmspannung") is the sum of this quantity, the irregular fall of potential due to the usually unknown and changing resistance of the solution, and the anode potential, which, in turn, depends upon the mixture of anions present and the current density at the anode. Hence this total

difference of potential is a quantity which has no important significance unless all these circumstances are stated, and they usually are not stated in descriptions of analytical electrolytic methods. On the other hand, the current density is easily found, being simply the current strength in amperes divided by the area of cathode, usually expressed in square decimeters.

Thus, other conditions being equal, the possible speed of quantitative electrolytic precipitation increases directly as the area of the electrode and also approximately as the concentration in the electrolyte of the substance to be deposited.

Yet another circumstance must be taken into consideration in this connection, namely, the nature and concentration of other cations present. A current density which will yield a perfectly pure coherent deposit of copper when no impurities besides acid and zinc, for example, are present, will cause the copper to be seriously contaminated with another cation, such as arsenic, whose deposition-potential is nearer that of copper. Moreover, obviously, the greater the concentration of the foreign cation, the more danger is there of depositing it with the copper.

Finally, since only the substance in the immediate vicinity of the electrode can be deposited, and the diffusion of new substance into this vicinity is a slow process, it is clear that thorough agitation of the solution will greatly increase the permissible speed of precipitation by supplying fresh ionized copper to take the place of that deposited far faster than diffusion can supply it. This has been pointed out by Foerster and Seidel,[1] by Richards, Collins and Heimrod,[2] and others. Gooch and Medway,[3] and Exner,[4] working under E. F. Smith, have shown how greatly the maximum current density is raised, if artificial means is employed to stir the liquid.

In summing up the conditions which determine the speed of precipitation of a given cation in a pure state, the following are seen to be the essential ones: The area of the cathode, the concentration of the solution, the nature of the other cations present and their concentration, and the rate of circulation of the electrolyte.

[1] *Ztschr. anorg. Chem.*, **14**, 106 (1897).
[2] *Proc. Am. Acad.*, **35**, 131 (1899).
[3] Gooch and Medway: *Am. J. Sci.* (4), **15**, 320 (1903).
[4] Exner: This Journal, **25**, 896 (1903).

The method described in the present paper was planned so as to gain the greatest possible advantage from the adjustment of the first two of these conditions, the others being fixed by the conditions of the experiment. The solutions analyzed contained no metal besides copper which was more easily deposited than hydrogen, therefore hydrogen formed the convenient and well-known safety-valve, preventing the precipitation of other metals after the copper had been all deposited; and an admixture of hydrogen alone was to be feared. Diffusion and automatic convection, caused by gas bubbles, were alone depended upon to cause circulation, on account of the complexity introduced by mechanical stirring.

The essential adjustment of the variable conditions consisted in decreasing, as much as possible, the volume of the solution, and increasing, as much as possible, the surface of deposition. By spreading the concentrated solution in a thin film between two platinum electrodes, the result was easily attained. The most convenient form of apparatus consisted of a pair of concentric platinum crucibles or dishes, the annular space between them serving to contain the film of electrolyte. The vessels were prevented from touching one another by a suitably shaped construction of fine glass rod, looking like a miniature inverted tripod. For ordinary analytical processes where only the fraction of a gram of metal is precipitated, crucibles are large enough.

The actual space between the crucibles in our trials measured 5 milliliters,[1] and the liquid to be analyzed was measured from a standard solution with a carefully made Ostwald pipette[2] of this volume. To prevent loss by spattering, a milliliter of the best kerosene was added to the surface of the electrolyte.[3] The outer crucible (the cathode) was connected in the usual way; the inner anode crucible was prevented from floating by being filled with pure water, and was connected to the battery by simply touching its interior with a platinum wire. The immersed area of the cathode was about 33 sq. cm.

[1] The word *milliliter* is used here instead of its cumbrous counterpart *cubic centimeter* because the standard of volume has recently, by international co-operation, been decided as the liter and not the cubic decimeter. The difference between the two is indeed slight, but since both precision and brevity are in favor of the word milliliter, it seems advisable. See this Journal, **26**, 413 (1904).

[2] Ostwald-Luther: *Phys. chem. Mess.*, p. 135 (1902).

[3] This device was probably first used by Allerton Cushman in some experiments upon electrolyzing nickel in this laboratory in 1898.

In our experiments a solution of cupric sulphate of about molar strength was used as the standard solution. The solution was slightly acidified to prevent the formation of cuprous oxide at first. If the area of the cathode had been 100 sq. cm., this would have permitted a current strength of 2 amperes,[1] but the cathode being only a third of this area, a current strength of 0.7 ampere should not be exceeded. As the copper is removed, the solution soon becomes so dilute that unless the current density is diminished, hydrogen will begin to appear, and the copper will be spongy. The area remaining unchanged, the current density is easily lessened by diminishing the current strength. It was found most convenient to arrange a current strength somewhat smaller than the maximum at the start so that a third of the copper present was precipitated in ten minutes, and then to diminish the current strength to two-thirds of its former value, thus proceeding gradually, adjusting the current strength to the concentration, until so much of the copper was precipitated that all danger of forming spongy copper was past. If, in a first analysis the amount of copper is not approximately known, the second, at least, may be carried out rapidly in this way. In order to illustrate this procedure, the following table may be given, showing the calculated amounts for each period.

Periods (each 10 minutes).	Current for 10-minute periods (ampere).	Calculated weight. Weight of copper precipitated.
1	0.60	0.118
2	0.41	0.081
3	0.27	0.063
4	0.19	0.037
5	0.12	0.024
6	0.08	0.016
Residue still remaining in solution, and precipitated in 15 minutes by current of 0.06 ampere		0.0126
Total copper found		0.3416

The deposit was beautifully bright and lustrous, and was washed and dried with the greatest ease. The complete electrolysis demanded only one and one-quarter hours.

For a convenient table, designed for such calculations, see Küster, Log. Rechentafel, p. 45 (1904).

Four successive analyses thus conducted gave the following weights of copper: 0.3416, 0.3418, 0.3415, 0.3416; average, 0.3416.

[1] Richard, Collins and Heimrod: *Proc. Am. Acad.*, **35**, 148 (1899).

The shortest time was an hour and a quarter for the total. The same volume of standard solution, analyzed in dilute solution of 25 milliliters, gave 0.3418 as an average of two analyses; but five hours were needed to free the electrolyte from copper as effectually as had been possible with the concentrated solution in a quarter of the time. It is easily seen that the time of analysis is approximately proportional to the volume of electrolyte, other conditions being equal.

The chief difficulty in this method lies in the trouble of adjusting the current strength every ten minutes. For this reason it seemed to us worth while to test an automatic device for the purpose. We found that this was very simply arranged by using a storage cell at 1.9 volts as the source of electromotive force. The effective electromotive force is, of course, the difference between this value and that of the copper-oxygen couple; and because this difference diminishes with the diminishing concentration of the copper solution, the current strength and hence the current density will also diminish.[1] The diminution in the given instance does not exactly correspond to the values required by theory, but, practically, it is found to serve every purpose. The actual current strengths at successive periods, measured by an amperemeter of very low resistance placed in the circuit, were as follows: At the beginning, 0.50 ampere; after ten minutes, 0.32 ampere; after twenty minutes, 0.28 ampere; after an hour, 0.11 ampere; after an hour and a half, 0.03 ampere. This minimum current was maintained without change until the close of the electrolysis in three hours. In this way three successive trials of the apparatus yielded each 0.3416 gram of lustrous copper. In no case was enough copper found in the residual electrolyte to give a visible precipitate with ferrocyanide, even in a special case where this electrolyte was ten times normal in concentration of acid. A much stronger solution or the presence of nitric acid would probably cause estimable traces of copper to remain in solution, however.

Although the more recent work of Gooch and Medway, and of Smith and Exner, diminish the importance of this method as a

[1] This device has since been used by Denso (*Ztschr. Electrochem.*, **9**, 463 (1903)) and probably others also have thought of it. In our arrangement it is particularly effective, because the resistance of the electrolytic cell is very small. Our experiments were made in 1901.

means of gaining time in electrolysis, it is, nevertheless, possible that some analysts who wish to avoid the trouble involved in effecting mechanical circulation may find the method convenient. At least it is of interest theoretically, in that it demonstrates the gain which may be made by adjusting two of the essential conditions in the most favorable way.

In conclusion, the contents of the paper may be summarized as follows:

The consideration of the conditions necessary for speed in quantitative electrolytic precipitation shows that among the essential ones are the concentration of the solution and the area of the electrode. In the method described, these conditions are made as favorable as possible by concentrating the electrolyte and placing it between two large surfaces in a thin film, such as the annular space between two crucibles separated by a tripod-like device of thin glass rod. Copper was the metal used to test this apparatus. As the concentration of the electrolyte diminishes during the electrolysis, the current strength is diminished, either in steps by the operator, or automatically by employing a single storage cell without resistance. The time required for complete precipitation is inversely proportional to the concentration of the solution, if the cathode surface is unchanged.

THE ELECTROLYTIC PREPARATION OF CHLOROFORM FROM ACETONE.

By J. E. Teeple.

Received March 4, 1904.

In a recent article[1] a method was given by which almost the theoretical yield of iodoform could be obtained by the electrolysis of a potassium iodide solution in the presence of acetone. No diaphragm was necessary, the essential feature being the gradual addition of a substance such as hydrochloric acid, hydriodic acid, or still better, iodine, to neutralize the excess of potassium hydroxide as fast as it formed. The temperature was kept below 25°, the electrolyte was thoroughly stirred, a high current density used at the cathode and a comparatively low current density at the anode. In short, the aim was to keep the conditions always favorable for the production of a maximum amount of hypoiodite.

[1] This Journal, **26**, 170 (1904).

It will be remembered that Schering's patent covered the electrolytic preparation of chloroform as well as bromoform and iodoform, from alcohol, aldehyde or acetone; but, so far as I know, there is no statement in chemical literature that chloroform has really been made electrolytically from any of these. In fact, Elbs and Herz[2] could not make it from alcohol. Nevertheless, it was reasonable to suppose that it could be made rather easily from acetone, and that the method which had been used for iodoform could be applied in nearly all details to the preparation of chloroform. This has been found to be the case. The present paper records some of the details regarding the preparation of chloroform by this method.

Assuming the problem to be the same as that presented in the case of iodoform, the solution of it consisted simply in electrolyzing a solution of a chloride in the presence of acetone under conditions that would continuously give the greatest possible yield of hypochlorite. These conditions are now quite well known from the work of Oettel, Förster, and others, the most important ones for our purpose being a temperature below 25°, a solution containing no alkali or as little as possible, a high current density at the cathode and a comparatively low one at the anode.

Preliminary experiments showed that the electrolysis of a 20 per cent. solution of potassium chloride or sodium chloride, containing acetone, for 10 to 15 ampere-hours at 15° to 20° does give small amounts of chloroform. By distilling the electrolyte with steam a layer of perhaps 1 cc. of chloroform is obtained in the distillate, provided evaporation has been prevented during the electrolysis and only a small amount (not over 5 cc.) of acetone has been added. Still better, using only 100 cc. of electrolyte and only 1 cc. of acetone, a small layer of chloroform is obtained in the distillate after only 2 or 3 ampere-hours; but no simple method suggested itself by which even an approximate determination of the chloroform could be made in the presence of the acetone. Consequently, it was decided to follow the progress of electrolysis by indirect determinations of the chloroform, for this purpose making use of the amount of alkali set free in the chloroform production.

[1] D. R. P. 29,771, March 7, 1884; Friedländer: "Fortschritte der Theerfarbenfabrikation," I, 576.

[2] *Zischr. Elektrochem.*, **4**, 118.

When an electric current is passed through a solution of sodium chloride, the sodium set free at the cathode reacts with water to form sodium hydroxide, and this latter then combines with the chlorine liberated at the anode to form chloride, hypochlorite, chlorate or perchlorate; also, the chlorine may decompose water, forming hydrochloric and hypochlorous acids. But in all these reactions the solution, as a whole, remains neutral,[1] provided there is thorough stirring, so that no chlorine gas escapes. If acetone is added to the solution, however, most of the hypochlorite reacts with it, possibly as follows:

$$6NaOH + 6Cl = 3NaOCl + 3NaCl$$
$$3NaOCl + CH_3COCH_3 = CCl_3COCH_3 + 3NaOH$$
$$CCl_3COCH_3 + NaOH = CHCl_3 + NAC_2H_3O_2;$$

so that for every gram-molecule of chloroform produced, 2 gram-molecules of sodium hydroxide remain in solution, and from a titration of the alkalinity of the solution the amount of chloroform formed may be determined.

This, of course, assumes that chloroform is the only product of the reaction; there are small quantities of other chlorine substitution products formed, so it would be more nearly correct to say that the amount of alkali present indicates the amount of current action which has affected the acetone, as opposed to that which has caused chlorate formation, reduction of hypochlorite, water decomposition liberating oxygen and other side reactions. The amount of alkali does not, however, measure the total current efficiency in the direction of chloroform formation, for if only small amounts of acetone are present, sodium hypochlorite may still be detected in the solution several hours after the electrolysis has ceased. Since this hypochlorite can react with the acetone to form more chloroform and liberate more alkali, it must also be taken into account in determining the total current efficiency.

To determine this total amount of current action directed toward the formation of chloroform three methods were tried: First, to a definite portion of the electrolyte an excess of acetone was added. The mixture was allowed to stand a few minutes and then the alkali present was determined by titration, using phenolphthalein as indicator; second, to a definite portion potassium iodide solution was added and, as soon as the iodine color

[1] A 15 per cent. sodium chloride solution electrolyzed one hour at 4 amperes was not alkaline to trinitrobenzene.

had disappeared, the alkali was determined as before. In either case one-half the number of gram-molecules of alkali found represents the gram-molecules of chloroform produced. In the third method, which seemed preferable to either of the preceding, the amount of hypochlorite was determined in one portion by acidifying, adding potassium iodide, and titrating with thiosulphate, and the alkali present was determined in another portion by titrating directly, using trinitrobenzene as indicator. One-third the amount of hypochlorite plus one-half the amount of alkali in gram-molecules represents the gram-molecules of chloroform.

It was by no means easy to find an indicator suitable for use in titrating the alkali in the last method. Trinitrobenzene was finaaly selected. It is colorless in acid solution, blood-red in alkaline, and is scarcely at all effected by chlorine or hypochlorites, but if left for a short time in a solution containing much alkali, it becomes permanently colored; hence the first part of the titration should be performed rather rapidly.

The following was found to be a convenient way of arranging an experiment to determine the amounts of chloroform produced and to show how the accumulation of alkali, if allowed to proceed, greatly decreased the yield. A large cylindrical dish provided with an efficient stirring apparatus and cooled by running water serves as a bath; into this 700 cc. water, 120 grams sodium chloride and 25 cc. acetone (if the stirring evaporates much acetone, more may be added at regular intervals) are placed and stirred till the salt has dissolved. The anode is a platinum foil of about 75 sq. cm., placed at one side of the dish; a platinum wire dipping just below the surface of the solution in the middle or opposite side of the dish acts as cathode. An ammeter and voltameter are connected in circuit, the solution is kept at a temperature of about 20°, and a current of 3 to 4 amperes passed through. At ten-minute intervals three 5 cc. portions are removed from the solution with pipettes. To the first a few drops of alcoholic trinitrobenzene solution are added and the solution titrated at once with tenth-normal acid till just colorless. The second is acidified, a little potassium iodide solution added and then it is titrated with tenth-normal thiosulphate. To the third a little potassium iodide solution is added and, as soon as the iodoform has precipitated, a drop of phenolphthaleïn is added, and the mixture is titrated with tenth-normal acid till colorless.

From the first titration the total amount of alkali present in the solution is computed; from the second, the amount of hypochlorite which has not yet reacted with acetone is determined; two-thirds the number of cubic centimeters of thiosulphate required represents the amount of tenth-normal alkali, which would have been formed had all the hypochlorite had time to react with the acetone. The third serves as a check and the number of cubic centimeters required for it should be aproximately two-thirds the thiosulphate used in the second, plus all the acid used in the first titration; this sum represents the total current action in the direction of chloroform formation. If no reactions occurred during the electrolysis, but the formation of hypochlorite and conversion of this into chloroform, then 12.43 cc. of normal alkali would be formed in the solution for each ampere-hour. The ratio between the amount actually found in the third titration (or the first and second combined) and the amount computed (12.43 times the number of ampere-hours) is taken to represent the current efficiency. During the first few minutes this efficiency is 80 to 90 per cent., but as the alkalinity of the solution increases it falls rapidly, so that during the fifth ampere-hour it is less than 40 per cent. and during the twelfth less than 10 per cent.

If now another experiment is arranged like this in all details except that after each titration with trinitrobenzene as indicator, there is added to the electrolyte nearly enough normal (2 N or 3 N) hydrochloric acid to neutralize the free alkali found, the current efficiency is very much increased, the average found for the first 8 ampere-hours being nearly 80 per cent. These experiments were made without the addition of $CaCl_2$ or K_2CrO_4 to the electrolyte, either of which would have increased the efficiency, but would, at the same time, have interfered with the titrations. Platinized electrodes, instead of the platinum ones used, might have increased the yield without any accompanying disadvantage.

Another method used to follow the course of the chloroform formation was to electrolyze about 100 cc. of a 20 per cent. salt solution containing 2 to 5 cc. of acetone and a few drops of an acetone solution of trinitrobenzene. Thorough stirring was accomplished either in the usual manner or with a rotating anode, and a strong standard (2 to 3 times normal) solution of hydro-

chloric acid was added from a burette, drop by drop, as needed to keep the electrolyte nearly neutral. If care is used to avoid an excess of alkali, the indicator works very satisfactorily. When the electrolysis is ended, however, the amount of acid used indicates only that portion of the reaction, which is entirely completed, and does not take into account the hypochlorite still present in solution. To determine the total current efficiency, as in the previous experiment, this hypochlorite must be determined directly, or potassium iodide solution or an excess of acetone must be added and a determination made of the amount of alkali set free. In this way the yield of chloroform is, as before, usually found to be nearly 80 per cent. of the theoretical yield.

As was previously stated, the hypochlorite reacts with acetone much slower than does hypoiodite. While hypochlorite may be detected for several hours in the presence of acetone (possibly the reaction product, chloroform, must also be present), if we add a little potassium iodide solution both hypochlorite and hypoiodite disappear within a minute. The rapidity with which the hypochlorite reacts is, of course, influenced by the amount of acetone present, the degree of alkalinity of the solution, and the temperature. In the experiments quoted above, using a large amount of solution and keeping the electrolyte neutral, the concentration of sodium hypochlorite did not vary far from 2 grams per liter. While possibly not accurate enough for use in determining the reaction velocity of chloroform-formation, the following experiment gives an approximate idea of the speed. Pass a current of 1 to 2 ampere-hours through 150 cc. of a 25 per cent. sodium chloride solution containing 5 cc. acetone and a little trinitrobenzene indicator; the bath is to be placed in running water at fairly constant temperature and stirred thoroughly. Add standard hydrochloric acid to the solution from time to time, as needed to neutralize the sodium hydroxide formed and when the electrolysis ends have the solution just neutral. Use a small portion to determine the amount of hypochlorite present, and continue the stirring and addition of acid to the rest as the red color due to alkali reappears. It can be followed quite well usually for about an hour, then proceeds quite slowly, but the red color will still reappear after four or five hours.

While the above methods of electrolyzing in open dishes, neu-

tralizing the alkali formed by additions of hydrochloric acid, and following the reaction by titration, either of the whole solution or of small portions, are quite satisfactory for determining the most favorable conditions and the efficiency, they obviously are not adapted to the isolation of the chloroform prepared. If we cover the dishes as closely as possible, chloroform may be distilled from the solutions after electrolysis, but better results can usually be obtained as follows:

In an ordinary cylinder of 150 to 200 cc. capacity place 100 cc. water, 20 grams sodium chloride and 4 cc. acetone; a platinum cylinder serves as anode and a platinum wire as cathode; close the vessel with a cork connected with a reflux condenser, cool the apparatus with running water and electrolyze, passing in a slow stream of chlorine as needed to neutralize the alkali, anode current density about 6 amperes per sq. dm. or less. After 8 to 10 ampere hours a small layer of chloroform may be removed from the bottom of the electrolyte by a pipette and more may be obtained by distilling the solution with steam. The amount of chloroform obtained, as pointed out, does not represent the whole current action in that direction, nor is it the whole of the chloroform actually formed, for a considerable part is still held in solution by the acetone; but if the process were run continuously on an industrial scale there would be no loss from either of these sources.

Before the electrolytic work described above was begun, a few experiments were made concerning the action of chlorine on solutions of sodium, potassium and calcium hydroxides containing acetone. The first two gave rather unsatisfactory yields of chloroform, due to chlorate formation, but calcium hydroxide gave quite good results. For example 9.3 grams of pure lime were slaked, suspended in 75 cc. water, 7 cc. acetone added, and a slow current of chlorine passed through. The vessel containing the mixture was kept cool and shaken thoroughly at frequent intervals. A layer of 4.4 cc. chloroform separated and 0.4 cc. more could be distilled off with steam, making 4.8 cc. or about 7.2 grams actually separated from the solution; computed, 9.9 grams from the equation,

$$4CaO + 12Cl + 2C_3H_6O = 3CaCl_2 + Ca(C_2H_3O_2)_2 + 2CHCl_3.$$

This would suggest electrolysis of a calcium chloride solution in

the presence of acetone as the best method of forming chloroform, if some way were found to overcome the high resistance due to the deposits forming on the cathode.

CORNELL UNIVERSITY,
February, 1904.

RUTHENIUM. V. THE CHLORIDES (Continued).

BY JAS. LEWIS HOWE.

Received March 17, 1904.

IN A previous paper upon the chlorides of ruthenium[1] there were described cesium and rubidium chlorruthenates, Cs_2RuCl_6 and Rb_2RuCl_6, and a so-called cesium "aquo" chlorruthenate, but at that time little had been learned of the conditions of formation of these salts. While no light has been thrown upon the peculiar origin of the particular chlorruthenates described in that paper, further study has shown a general method by which the chlorruthenates, $X_2Ru^{IV}Cl_6$, as well as the "aquo" chlorruthenates, can be prepared.

When a solution of ruthenium trichloride, prepared by the action of hydrochloric acid on either ruthenium tetroxide or the hydrated sesquioxide (that is, the ordinary ruthenium chloride) is boiled in very dilute solution with hydrochloric acid and alcohol, it gradually changes from its deep yellowish red color to a lighter and less yellow tint. If now it is evaporated with an alkaline chloride, it deposits crystals which may vary from the rose prisms described in the previous paper, to rich red crystals, somewhat resembling the ordinary crystals of the chlorruthenite ($X_2Ru^{III}Cl_5$), but lighter in color and transparent. This change may be induced by other agents than alcohol, as oxalic acid and possibly stannous chloride. These crystals are the "aquo" chlorruthenate, the cesium salt of which was described in the previous paper. Their formula is $X_2RuCl_5H_2O$, but to distinguish them from the ordinary hydrated salts of the chlorruthenites, the formula may be written $X_2Ru(OH_2)Cl_5$.

The "aquo" chlorruthenates differ very markedly from the isomeric chlorruthenites. They are stable to 140°, but lose water rapidly at 180°, leaving the salt X_2RuCl_5. Crystals of the dehydrated potassium "aquo" chlorruthenate preserve the form of the

[1] This Journal, **23**, 775 (1901).

aquo salt, with often fine reflecting surfaces, but except in thin sections, are opaque. Their solution differs wholly from that of the potassium chlorruthenite, with which it is isomeric, and gives the reactions for the original aquo salt. We thus appear to have two distinct salts of the formula X_2RuCl_5. In what the nature of this isomerism consists, we can hardly conjecture. It should be mentioned that while the ordinary potassium chlorruthenite is anhydrous, Miolati[1] has obtained monohydrated crystals, K_2RuCl_5,H_2O, which are thus isomeric with, but distinct from, the aquo salt.

Mr. C. S. Lind[2] was kind enough to compare the conductivity of the solutions of the chlorruthenite and the "aquo" chlorruthenate, and I am permitted to quote from his results. Both salts undergo a similar decomposition in water, accompanied by an increase in conductivity, but this increase is much slower in the case of the aquo salt. While the initial value of the conductivity is the same for the two salts, the final value for the aquo salt is much less than that for K_2RuCl_5. The final value for the latter corresponds to the equation

$$K_2RuCl_5 + 2H_2O = 2KCl + 2HCl + Ru(OH)_2Cl,$$

while the final value for the aquo salt approximates closely to the equation

$$K_2RuCl_5 + H_2O = 2KCl + HCl + Ru(OH)Cl_2$$

or

$$K_2Ru(OH_2)Cl_5 + H_2O = 2KCl + HCl + Ru(OH_2)(OH)Cl_2.$$

The most distinguishing reaction of the aquo salt is that its solution is immediately darkened by the fumes of chlorine or bromine. This affords a ready means of identification, as the reaction is possessed by no other class of ruthenium salts as far as known. This reaction is caused by the formation of the chlorruthenate, X_2RuCl_6 (or bromruthenate).

This then affords us a simple means of preparing the chlorruthenates. Through a cold, concentrated solution of the "aquo" chlorruthenate, preferably with considerable excess of hydrochloric acid, is led a rapid stream of chlorine. The solution immediately darkens, becoming intense brown with a yellowish cast, and, if sufficiently concentrated, the chlorruthenate is precipitated in minute black octahedra. After being dried on a tile, the dark

[1] Miolati and Taziuri: *Gazz. chim. ital.*, **30**, II, 511 (1901).

[2] C. S. Lind: Thesis, Mass. Inst. Tech., 1902.

crystalline powder has a peculiar greenish sheen, which is unique among the halide compounds of ruthenium, and which serves to identify the salt, if moderately pure.

The potassium, ammonium, rubidium, and cesium chlorruthenates, K_2RuCl_6, $(NH_4)_2RuCl_6$, Rb_2RuCl_6, and Cs_2RuCl_6, have been thus prepared, as well as several bromruthenates, which will be described in a later paper. The method of preparation is thus general. In the case of the very sparingly soluble rubidium and cesium salts the preparation is easy; for the more soluble potassium salt, considerable concentration of solution is necessary, while for the ammonium salt the conditions must be carefully adjusted, both in view of the decided solubility of the salt, and the action of the chlorine upon the ammonium. Though succeeding once in preparing a salt which was nearly pure, other attempts resulted in failure.

The series of chlorruthenium salts thus far known is as follows:

[1]Na_2RuCl_5			
[1]K_2RuCl_5	[2]K_2RuCl_5,H_2O	$K_2Ru(OH_2)Cl_5$	[4]K_2RuCl_6 [illegible]
[1]$(NH_4)_2RuCl_5$		$(NH_4)_2Ru(OH_2)Cl_5$	$(NH_4)_2RuCl_6$
	Rb_2RuCl_5,H_2O	[3]$Rb_2Ru(OH_2)Cl_5$	Rb_2RuCl_6
	Cs_2RuCl_5,H_2O	$Cs_2Ru(OH_2)Cl_5$	Cs_2RuCl_6

		[6]$Na_2Ru(NO)Cl_5,3H_2O$
	[5]$K_2Ru(NO)Cl_5$	[6]$K_2Ru(NO)Cl_5,2H_2O$
	[5]$(NH_4)_2Ru(NO)Cl_5$	[6]$(NH_4)_2Ru(NO)Cl_5,2H_2O$
$Rb_2RuO_2Cl_4$	$Rb_2Ru(NO)Cl_5$	$Rb_2Ru(NO)Cl_5,2H_2O$
$Cs_2RuO_2Cl_4$	$Cs_2Ru(NO)Cl_5$	$Cs_2Ru(NO)Cl_5,2H_2O$.

In addition to the above, several other salts have been described, which are not well defined and may be mixtures.

It is interesting to note that Wintrebert[7] has prepared salts of the series $X_2OsO_2Cl_4$, called by him osmyl chlorides, which correspond to the series $X_2RuO_2Cl_4$, which I have called oxychlorruthenates. The nomenclature I have used in my papers is open to the criticism of being inconsistent, but it has been transitional; I have delayed proposing a consistent nomenclature until the salts of bivalent ruthenium could be prepared, a hope that seems near realization. Wintrebert has also described salts of the type

[1] Claus.

[2] Miolati: *Loc. cit.* Verified by H. B. Graybill in this laboratory.

[3] A later examination has shown that the salt from which analysis 18 (this Journal, 23, 786) was made, was the "aquo" chlorruthenate.

[4] Antony.

[5] Described by Claus as K_2RuCl_6 and $(NH_4)_2RuCl_6$. Correct composition shown by Joly.

[6] Joly.

[7] Wintrebert: Thesis, Bordeaux, 1902.

$X_2OsO_3Cl_3$, no ruthenium analogues of which have as yet been prepared.

Reference should be made to the first chlorruthenate, K_2RuCl_6, which was prepared by Antony, and which from its properties appears to belong to a different series from the chlorruthenates prepared by the action of chlorine upon the "aquo" chlorruthenates. As the description of this salt and its preparation has not appeared in a readily accessible journal, I venture to translate the description which Professor Antony was kind enough to write out for me in detail.

"I have prepared the chlorruthenate of potassium, by heating to fusion 6 parts of sodium hydroxide with 1 part of absolutely pure ruthenium; small portions of potassium chlorate were added till the ruthenium was completely dissolved. The melt was then heated until the excess of chlorate was wholly decomposed, and allowed to cool. Very dilute hydrochloric acid was then added, the whole being kept cold. If the chlorate has been completely decomposed, there is no evolution of ruthenium tetroxide. The liquid cannot be warmed without decomposition, but when evaporated in a vacuum over sulphuric acid, it deposits red-brown crystals of the chlorruthenate, almost insoluble in the potassium chloride solution, somewhat soluble in cold water, and very soluble with decomposition in warm water. Analysis gave the following figures:

	Found. Per cent.	Calculated for K_2RuCl_6. Per cent.
Chlorine (with ruthenium).....	36.074	36.109
KCl	37.936	37.993
Ruthenium	25.912	25.897
Total chlorine.....	54.146	54.163."

It will be noted that the two chlorruthenates differ in color and solubility, that of Antony being red-brown and only slightly soluble in cold water, while that which I have prepared is black with a greenish sheen, and is very soluble and rapidly decomposed by cold water. It appears with our present light as if there were among the chlorides of ruthenium three pairs of isomers, *viz.*:

K_2RuCl_5,H_2O	Monohydrated chlorruthenite,
$K_2Ru(OH_2)Cl_5$	"Aquo" chlorruthenate;
K_2RuCl_5	Chlorruthenite,
K_2RuCl_5	Dehydrated "aquo" chlorruthenate;
K_2RuCl_6	Chlorruthenate from K_2RuO_4+HCl,
K_2RuCl_6	Chlorruthenate from $K_2Ru(OH_2)Cl_5+Cl$.

EXPERIMENTAL PART.

The analyses of the following salts were carried out as has been described in the previous paper.

Potassium Aquochlorruthenate, $K_2Ru(OH_2)Cl_5$.—Prepared by boiling a slightly acidified (with HCl) solution of K_2RuCl_5 with alcohol, or the hydrated sesquioxide, Ru_2O_3, with hydrochloric acid and alcohol. The complete conversion of the salt requires several hours' boiling and is noticeable by the solution becoming much lighter in color and losing all trace of a yellowish cast, having a clear rose-red shade. The salt crystallizes, on evaporation, in apparently orthorhombic octahedra, showing often base and prism faces. It is quite soluble in water, bearing considerable dilution before slowly hydrolyzing. On boiling, the solution darkens to a greenish brown, but gives no immediate precipitate. This darkened solution does not change immediately on addition of hydrochloric acid (distinction from the chlorruthenates) but gradually becomes yellower with a cast of red. The characteristic reaction of the salt is the immediate darkening of its solution on addition of bromine or chlorine water. With alkalies its solution gives a dirty white precipitate which soon becomes black, differing thus from the solutions of the trichloride, which give an immediate black precipitate. The other reactions of the salt, as far as examined, are common to all ruthenium chloride solutions.

(1) 0.3927 gram salt. Lost no water at 90°.

(2) 0.4792 gram salt. The water in this analysis was determined by absorption in a P_2O_5 tube, the salt being heated in a stream of air, and a coil of silver being used to hold the chlorine evolved.

(3) 0.4335 gram salt. The loss of water by the desiccator-dried salt was as follows:

	Gram.
100° 24 hours	0.0005
140° 24 hours additional	0.0008
180° 3 hours	0.0167
180° 4 hours additional	0.0039
180° 18 hours additional	0.0003

The salt is thus stable up to 140°, but loses its water between 140° and 180°.

	(1) Per cent.	(2) Per cent.	(3) Per cent.	Theory. Per cent.
Ruthenium	26.84	26.84	....	27.09
Chlorine (with ruthenium)	27.78	....	....	28.35
Potassium	20.63	21.13	....	20.85
Chlorine (with potassium)	18.67	19.14	....	18.90
Water	....	6.07	4.82	4.80

Ammonium Aquochlorruthenate, $(NH_4)_2Ru(OH_2)Cl_5$.—Prepared by boiling $(NH_4)_2RuCl_5$ with dilute acidified alcohol. The crystals obtained on evaporation were far from uniform and it was difficult to get satisfactory material for analysis. The only satisfactory method of analysis was heating the salt with lime and determining the chlorine by dissolving out the $CaCl_2$ formed. There seems to be some evidence of the presence of a salt, $NH_4Ru(OH_2)Cl_4$ (*i. e.,* $NH_4Cl,Ru(OH_2)Cl_3$), as in several analyses ruthenium to the amount of about 37 per cent. (theory 36.39 per cent.) was found, but the existence of this salt could not be established. All the solutions showed the aquo salt reaction with bromine.

(4) 0.4400 gram salt. By lime method.

(5) 0.2537 gram salt. Stable at 145°; lost in 34 hours at 200° 0.0120 gram; in 24 hours further heating 0.0025 gram; no further loss on heating at 200°.

	(4) Per cent.	(5) Per cent.	Theory. Per cent.
Chlorine	52.12	....	53.25
Water	....	5.79	5.41

Potassium Chlorruthenate, K_2RuCl_6.—Prepared by the action of chlorine on concentrated, acid solution of $K_2Ru(OH_2)Cl_5$. Minute black octahedra, with greenish sheen. Easily soluble and rapidly decomposed by water, giving pale purplish brown solution on boiling, which is given a fugitive deep purple by addition of concentrated hydrochloric acid. This is the only characteristic reaction which has been found for the chlorruthenates. Dilute solution in hydrochloric acid is pure yellow, concentrated solution deep yellowish red.

(6) 0.2585 gram salt.

	(6) Per cent.	Theory. Per cent.
Ruthenium	25.85	25.89
Chlorine (with ruthenium)	34.82	36.13
Potassium	20.28	19.92
Chlorine (with potassium)	18.37	18.06

Ammonium Chlorruthenate, $(NH_4)_2RuCl_6$.—Prepared by action of chlorine on a concentrated solution of the aquo salt. Tile dried but very difficult to free from the mother-liquor. Resembles in every respect the potassium salt except that it is more soluble.

(7) 0.2129 gram salt. Considerable of the lower chloride present.

(8) 0.1543 gram salt. An attempt was made to separate the chlorine attached to the ruthenium by a hydrogen stream and let the ammonium chloride sublime on the tube. A little of the vapor of the ammonium chloride passed on and failed of absorption in the silver nitrate solution. The ratio Ru : Cl was 1 : 3.6, showing as in 7 (same crop of crystals) that considerable of the lower chloride was present.

(9) 0.4812 gram salt. Lime method. Ruthenium recovered and heated in hydrogen after solution of the lime.

	(7) Per cent.	(8) Per cent.	(9) Per cent.
Ruthenium	30.95	31.17	28.43
Chlorine (with ruthenium)	....	39.26	....
Chlorine (with ammonium)	....	18.78	....
Total chlorine	....	....	59.14

	Theory for $(NH_4)_2RuCl_6$. Per cent.	$(NH_4)_2RuCl_5$. Per cent.
Ruthenium	29.02	32.32
Chlorine (with ruthenium)	40.47	....
Chlorine (with ammonium)	20.23	....
Total chlorine	60.70	56.28

Cesium Chlorruthenate, Cs_2RuCl_6.—It is well to add this analysis of the salt prepared by the action of chlorine on a solution of the aquochlorruthenate.

(10) 0.3338 gram salt.

	(10) Per cent.	Theory. Per cent.
Ruthenium	18.06	17.51
Chlorine (with ruthenium)	22.21	24.44
Cesium	44.44	45.82
Chlorine (with cesium)	12.85	12.22

WASHINGTON AND LEE UNIVERSITY,
LEXINGTON, VA., March 10, 1904.

SOLUBILITY OF GOLD IN CERTAIN OXIDIZING AGENTS.[1]

By Victor Lenher.

Received March 16, 1904.

The inactive character of gold is so pronounced that towards many of the reagents the element is quite indifferent, in fact, almost the only solvents in general use for dissolving the metal are chlorine, bromine, or a solution of alkaline cyanide in presence of atmospheric oxygen. Chlorine and bromine attack the metal readily, while iodine only dissolves the metal when it is freshly liberated, or under other very favorable circumstances. The metallic perchlorides, perbromides and periodides, according to Nicklès,[2] dissolve gold, the lower halides of the metal being formed along with gold chloride. Hot selenic acid readily dissolves gold. Iodic acid has slight action on the metal, while, according to Prat,[3] a mixture of iodic and sulphuric acids dissolves gold when heated to 300°. This reaction has been verified by the author, who also finds that gold is readily soluble in a mixture of hot sulphuric and periodic acids.

Gold is also slightly soluble in the alkaline sulphides and thiosulphates.[4]

There is another class of substances, substances which evolve oxygen when treated with acids, whose action on gold has received very little attention.

Several years ago the author had occasion to review the work of Mitscherlich on the solubility of gold in selenic acid, and showed that gold is readily attacked by pure hot selenic acid with the formation of auric selenate.

In following the same line of work with telluric acid, which in many respects is closely analogous to selenic acid, the obstacle is met that telluric acid is a solid. This apparent difficulty can be obviated by first dissolving the crystalline telluric acid in sulphuric or phosphoric acid. Such a solution of telluric acid, when heated, dissolves metallic gold.

With the fact at hand that at the same temperature at which selenic acid or a solution of telluric acid attacks gold, the acids themselves are broken down into the dioxides and oxygen it ap-

[1] Read at the St. Louis meeting of the American Chemical Society.

[2] *Ann. Chim. Phys.* (4), X, 318.

[3] *Compt. rend.*, **70**, 840.

[4] Stedefelt: "Lixiviation of Silver Ores," pp. 15, 38.

peared probable that the solvent action in these cases was due to the production of oxygen in the reaction. Should this view be correct, gold should be soluble in acids when an oxidizing agent is present. The action of a large number of substances, such as oxides of various types, sulphates, etc., was tried on gold in presence of sulphuric, phosphoric and arsenic acids, and only such substances as give oxygen in presence of the acids will act on gold. In most cases, the only precautions necessary in order to demonstrate the solvent action is to have the acids in a high degree of concentration.

All of the substances that have been used in the following experiments were carefully tested for the halogens and only such substances used as were halogen-free. In many instances the substances had to be prepared in order to obtain them in a high degree of purity. The author wishes to acknowledge the services of Mr. Geo. Kemmerer, who greatly assisted the work at many points, both in preparing many of the substances used and in confirming the reactions.

The first substance that was naturally examined was manganese dioxide, as it is well known that manganese dioxide gives oxygen when heated with sulphuric acid. A mixture of manganese dioxide and sulphuric acid, when heated for a few minutes with gold, causes the metal to go into solution. On diluting the solution and testing with oxalic acid or ferrous sulphate, all of the gold is precipitated. In working with manganese dioxide and sulphuric acid, practically the only precaution necessary is to have the acid concentrated. Solution of gold in presence of manganese dioxide and sulphuric acid takes place readily when the mixture is hot, but the reaction also takes place in the cold. A mixture of manganese dioxide and sulphuric acid, when allowed to remain in contact with gold leaf for twelve hours at 0°, will dissolve sufficient gold to give an appreciable precipitation, when the mixture is diluted and treated with ferrous sulphate. It is thus seen that while heat accelerates the reaction, solution nevertheless takes place at low temperatures.

The higher oxides of manganese act in an entirely similar manner. The substances actually worked with were manganese dioxide (*a*) native, (*b*) from the ignition of manganese nitrate, (*c*) by the action of bromine on manganese acetate: Manganese

sesquioxide (Mn_2O_3), manganese protosesquioxide (Mn_3O_4), and potassium permanganate. The solvent action takes place in a similar manner when phosphoric or arsenic acid is substituted for sulphuric, but the action is greatly moderated.

In 1872 Allen[1] showed that when solid potassium permanganate and sulphuric acid are heated for a few minutes with precipitated gold the solution becomes nearly clear, and on diluting and testing with oxalic acid or ferrous sulphate the solution was found to contain abundance of gold.

This experiment has been repeated, using sulphuric acid as described by Allen, and also by substituting phosphoric for the sulphuric acid. In all cases solution takes place and the gold can be readily detected by ferrous sulphate.

Lead dioxide, lead sesquioxide and red lead, when used with sulphuric acid, cause gold to enter into solution. The action takes place more readily in the warm than in the cold, though at the ordinary temperatures solution does actually take place, gold being found in the solution after several hours' contact.

With the higher oxides of lead, phosphoric acid can be substituted for the sulphuric acid, solution being affected. With chromium trioxide, chromium tetroxide and nickelic oxide, solution of gold is effected in presence of sulphuric or phosphoric acids, the reaction taking place, though moderated, in the cold.

When nitric acid is subjected to heat, more or less decomposition is effected, part of the acid breaking down into nitrogen dioxide and oxygen. This reaction can be used in a highly satisfactory manner to demonstrate the solubility of gold in sulphuric acid in presence of an oxidizing agent. This reaction was first noted by Reynolds,[2] and later by Spiller.[3] The results which these chemists obtained have been confirmed by the author and show that when a mixture of hot nitric and sulphuric acids comes in contact with gold the metal enters into solution and, at the same time, a lower oxide of nitrogen is formed by the reduction of the nitric acid and this oxide remains in the solution.

That a lower oxide of nitrogen is present in the solution after the gold has dissolved can be demonstrated in a very pretty manner, as Spiller has shown, by adding the solution to water when

[1] *Chem. News*, **25**, 85.
[2] *Ibid.*, **10**, 48, 167, 277.
[3] *Ibid.*, **10**, 173.

the metal is thrown out as a purple precipitate. Allen[1] later showed that this precipitation by water from nitric-sulphuric acid solution is due to the presence of a lower oxide of nitrogen, probably nitrous acid, since when the water used for dilution contains potassium permanganate no precipitation takes place. Also ammonium sulphate destroys the nitrous acid and, after boiling with ammonium sulphate, no precipitation takes place, while when fuming nitric acid is added to any of the liquids, the gold is thrown down, purple in color. While Reynolds, Spiller, and Allen have studied the reaction of a mixture of hot nitric and sulphuric acids on gold, the influence of temperature on the reactions seems to have escaped their attention, and also that certain other acids as phosphoric acid can be substituted for the sulphuric acid with practically as great solvent action taking place.

While a mixture of nitric acid with either sulphuric acid or phosphoric acid readily acts on gold when warm, solution actually takes place, though more slowly, even at zero.

The action of oxygen gas on gold leaf, suspended in hot sulphuric acid, was also tried, but neither oxygen nor ozone would cause any of the metal to pass into solution.

The anode oxygen, obtained in electrolysis, was next studied as to its action on gold. Bunsen noticed, when using for the electro decomposition of water an apparatus in which the platinum electrodes were connected with the terminals by means of gold solder, that on electrolyzing in presence of dilute sulphuric acid there is a film of oxide formed on the gold. Later it was shown by Spiller that when a plate of metallic gold is made the anode and a piece of platinum foil or gauze used as the cathode in an electrolyte of sulphuric acid or a mixture of nitric and sulphuric acids, the gold anode dissolves and the metal was deposited on the cathode, the source of the current used being a few Grove cells.

This work, which has been repeatedly verified, demonstrates that in presence of strong sulphuric acid, solution of gold can be effected readily by means of anode oxygen, the action proceeding rapidly when the acid is hot. On the other hand, when the acid is dilute the oxide of gold formed does not pass through the solution and deposit on the cathode as metal, but remains as an incrusta-

[1] *Chem. News*, **25**, 85.

tion on the gold anode. Here again a similar series of results is obtained when phosphoric acid replaces the sulphuric. When solutions of the acid sulphates of potassium or sodium are used as electrolytes, the action goes on exactly as above indicated. If the solution contains sufficient free acid, gold passes through the electrolyte, while if the solution is dilute or contains only a little free acid, the oxide remains as a film on the anode.

In the case of an alkaline electrolyte, such as a solution of sodium or potassium hydroxide, it is possible for some of the gold to pass through the solution, probably from the formation of aurate of the alkali. Such is actually the case, although in alkaline solution a large amount of oxide remains as an incrustation on the gold anode employed. When neutral salt solutions are employed as electrolytes, such as the nitrates or sulphates of potassium or sodium, very little, if any, of the gold can pass through the electrolyte, and as a result the anode is converted into the oxide Au_2O_3. Here we have the last step in the series of experiments, *viz.*, obtaining the gold oxide in pure condition and retaining it as such.

In the above series of experiments the current used was 0.3-0.5 ampere at a pressure of 5 volts, the anode being a sheet of gold and the cathode a 20-gram platinum crucible. In such experiments where gold was deposited on the crucible, the quickest method found for removing the metallic deposit, which frequently appeared as a hard plating, was found to be the hot mixture of nitric and sulphuric acids, as indicated above. This method was found to be vastly superior to that of the use of a cyanide solution, such as was at first used.

It thus appears that gold is not only attacked by the halogens, but is also readily attacked in a large number of reactions in which oxygen is produced, these latter reactions taking place readily in the warm solutions, but slowly even at as low a temperature as zero. Furthermore, it appears that it is necessary for the oxygen to be produced in the mixture and that ordinary oxygen gas, when conducted into sulphuric acid in which gold leaf is suspended, will not cause the gold to dissolve.

CHEMICAL LABORATORY,
UNIVERSITY OF WISCONSIN.

FORMS IN WHICH SULPHUR OCCURS IN COAL; THEIR CALORIFIC VALUES AND THEIR EFFECTS UPON THE ACCURACY OF THE HEATING POWERS, CALCULATED BY DULONG'S FORMULA.

By E. E. Somermeier.

Received February 3, 1904.

The estimation of the calorific value of coal from the ultimate analysis, involves the calorific value of the sulphur present. There is much difference of opinion among authorities as to what this value is, and where the amount of sulphur is large, as is often the case, the question becomes of importance, especially as to how the heating value is affected by the different forms in which sulphur may occur. The investigation of this question, some of the results of which are given in this paper, was undertaken at the suggestion of Professor N. W. Lord, to whom the writer wishes to acknowledge his indebtedness for valuable advice and suggestions.

Of the various formulas for determining the calorific value from the ultimate analysis, that of Dulong, $8080C + 34460(H - \frac{1}{8}O) + 2250S$ is, perhaps, the one most generally used. The calorific value of amorphous sulphur burned to sulphur dioxide is 2250 calories, that of the ordinary rhombic form is 2220 calories, but, as free sulphur of any kind occurs but rarely in unweathered coal in any considerable amounts, the value given for sulphur in this formula is necessarily only an approximation.

Sulphur occurs in coal in the form of pyrites, sulphates, organic sulphur and as free sulphur, but in all samples of coal tested in this investigation, pyrites and organic sulphur represented most of the sulphur present. Very little free sulphur was found and only small amounts of sulphates. One of the purposes of this investigation is to determine how closely the calorific values of the different forms of sulphur agree with the value, 2250 calories, given in Dulong's formula.

CALORIFIC VALUE OF PYRITES.

Pyrites is rarely or never entirely absent from coal, the amount present varying from a fraction of a per cent. up to 8 or 10 per cent., or even more. In most bituminous coals probably the greater part of the sulphur present in the coal is there in the form of pyrites. That the presence of the pyrites has an

important effect upon the heating power of the coal is a fact generally recognized, but authorities upon the calorific value of fuels are far from agreeing as to just what this effect is. Some apparently assume the heating power of pyrites to be merely that of an equivalent amount of free sulphur and neglect the iron entirely. Others apparently assume its heating power to be the same as that of equivalent amounts of free iron and sulphur. Both assumptions are arbitrary, and, as is shown by actual experiments, neither is true.

In order to investigate the actual heating value of pyrites, the following experiments were performed. A well crystallized specimen of pyrites, apparently free from oxidation or admixed impurities, was selected for the tests. This was finely powdered and thoroughly mixed. By analysis, it had the following composition: Fe, 46.50 per cent.; S, 53.2 per cent.; SiO_2, 0.45 per cent., = 100.15 per cent., which shows the sample to be very nearly pure FeS_2, the theoretical composition of which is Fe, 46.6 per cent.; S, 53.4 per cent.

Pyrites by itself does not burn completely in a calorimeter; in order to secure combustion it must be mixed and burned with some other substance having a high calorific intensity. Naphthalene and coal are two such substances. Coal was chosen, since pyrites can be more easily and thoroughly mixed with powdered coal than with naphthalene, and also, because the question to be investigated is the calorific value of pyrites in coal. The sample of coal selected was low in moisture, sulphur and ash. Analysis showed: Moisture 1.05 per cent., volatile matter 17.20 per cent., fixed carbon 75.70 per cent., ash 6.05 per cent., sulphur 0.54 per cent., nitrogen 1.38 per cent.

The following mixtures of the finely powdered coal and pyrites were made:

	(1)	(2)	(3)	(4)	(5)	(6)
Percentage of coal	90	85	80	60	50	50
" " pyrites	10	15	20	40	50	50

Accurately weighed briquettes of these were then burned in a Mahler calorimeter and the heat of the combustion of the mixtures determined. From the total heat developed in the calorimeter, the heat due to the combustion of the iron wire used as a fuse was deducted, and also 10 calories for the combustion of atmospheric nitrogen present in the calorimeter. This latter cor-

rection was found necessary, as will be shown later in this paper. The corrected results are as follows:

No.	Actual weight taken.								
(1)	0.8760 gm.	of coal	+	0.0973 gm.	of pyrites	=	7509	calories
(2)	0.8273	"	"	+ 0.1460	"	"	= 7227	"
(3)	0.7825	"	"	+ 0.1956	"	"	= 6996	"
(4)	0.5895	"	"	+ 0.3930	"	"	= 5888	"
(5)	0.4876	"	"	+ 0.4876	"	"	= 5262	"
(6)	0.4870	"	"	+ 0.4870	"	"	= 5155	"

Reducing these values to a basis of 1 gram of coal which, determined in the same way, has a calorific value of 8275 calories, we have:

1 gm.	of coal	+ 0.1111 gm.	of pyrites	= 8572	cal.	or 1 gm.	of pyrites	= 2673 cal.
1 "	"	+ 0.1765 "	"	= 8736	"	1 "	"	= 2612 "
1 "	"	+ 0.2500 "	"	= 8940	"	1 "	"	= 2660 "
1 "	"	+ 0.6666 "	"	= 9990	"	1 "	"	= 2573 "
1 "	"	+ 1.0000 "	"	= 10790	"	1 "	"	= 2515 "
1 "	"	+ 1.0000 "	"	= 10586	"	1 "	"	= 2311 "

As Nos. 4 and 5 gave results lower than those from 1, 2 and 3, formation of SO_2 was suspected, but a slow evolution of the gases of combustion from No. 6, through an alkaline solution of bromine, showed no sulphur, while at the same time the result obtained is much lower than Nos. 4 and 5, which themselves were suspected to be low. However, an examination of the magnetic residue, remaining after the combustion, showed the presence of a considerable amount of sulphur, and the quantitative results of later experiments justify discarding 4, 5 and 6 as being low on account of unburned ferrous sulphide in the residues, not, however, quantitatively determined. The average value for 1, 2 and 3 is 2648 calories.

To determine some of the reactions of the combustion the calorimeter, after a determination, was rinsed out six or eight times with water and the collected washings examined for total free acid, sulphuric acid and iron. The determination of the total free acid was made by titration with a standard solution of ammonia, using methyl orange as an indicator, the ammonia being added rather slowly and with constant stirring of the solution. The presence of ferric sulphate made the end-point somewhat indistinct as the color developed by that salt, as the solution approached neutrality masked the end-point and rendered it less

sharp and well marked. The formation of a very slight permanent precipitate of ferric hydroxide was taken as the final endpoint as titrations of standard acid solutions, containing approximately the same amounts of ferric sulphate, showed that working in this way results accurate to 0.1 cc. of standard ammonia could be obtained. A standard solution of ammonia, already made up in the laboratory for other purposes, was used. One cc. contained 0.005 gram of ammonia, equivalent to 0.0047 gram of sulphur as sulphuric acid, and to 0.0041 gram of nitrogen as nitric acid. The results of the tests upon the calorimeter washings are as follows:

	Gram of sulphur after deducting that in coal.	Gram of iron.	Gram of sulphur estimated as combined as $Fe_2(SO_4)_3$.	Gram of sulphur as free H_2SO_4 from pyrites.	Cc. of standard ammonia required to neutralize washings.	Estimated cc. of standard ammonia to neutralize free H_2SO_4 from pyrites.	Estimated cc. of standard ammonia to neutralize $H_2SO_4 + HNO_3$ from coal.	Cc. of standard ammonia to neutralize the HNO_3 from nitrogen of air.
(1)	0.0492	0.0030	0.0025	0.0467	16.0	10.0	3.9	2.1
(2)	0.0703	0.0045	0.0037	0.0666	20.0	14.2	3.7	2.1
(3)	0.0972	0.0065	0.0056	0.0916	26.0	19.5	3.5	3.0
(4)	0.1858	0.0095	0.0081	0.1777	42.0	37.8	2.7	1.5

The amounts of sulphur obtained from the calorimeter washings, after correcting for that present in the coal (0.54 per cent.), are given in the first column. These values run from 1 to 4 per cent. lower than the amount present in the pyrites (53.2 per cent.), but subsequent tests showed that more thorough washing of the calorimeter was necessary to obtain all the sulphuric acid present, while the presence of sulphur as ferrous sulphide in the magnetic residue, as is shown later, also accounts for a portion. The amounts of iron present in the washings are given in the second column. Calculating the iron present as ferric sulphate, the amounts of sulphur, so combined, are given in the third column.

The results given in the fourth column show the amounts of free sulphuric acid from the pyrites. They are obtained by deducting the sulphuric acid present as ferric sulphate from the total sulphuric acid, calculated from the first column. The total acidity is shown in the fifth column by the amount of standard ammonia required for neutralization. The sixth column represents the estimated amount of the standard ammonia required to

neutralize the amounts of free acid given in the fourth column. The coal used in the combustions contained 1.38 per cent. nitrogen and 0.54 per cent. sulphur, which, during the combustion, were burned to nitric and sulphuric acids. The amounts of acid formed from the nitrogen and sulphur present in 1 gram of coal would require 4.5 cc. of standard ammonia for neutralization. The estimated amounts, corresponding to the amounts of coal taken, are given in the seventh column. Subtracting the sum of the amounts given in 6 and 7 from the amount required to neutralize the total free acid, gives the values in the last column, which represent the amount of standard ammonia required to neutralize the nitric acid formed from the nitrogen of the air present during the combustion. These values indicate some oxidation of this nitrogen to nitric acid, the average of the four being 2.2 cc. of standard ammonia. Tests on the washings of the calorimeter, after the combustion of the coal alone, gave an average titration of 5.8 cc. of standard ammonia; deducting 4.5 cc., accounted for by the nitrogen and sulphur present in the coal, leaves only 1.3 cc. of ammonia required to neutralize the nitric acid formed by oxidation of nitrogen from the air in this case. This value is, however, too low, as no allowance was made for the acid, combined with the iron, as was done in the first case, the iron not having been determined. This correction would be small because it appears from the table that the amount of iron in solution increases with the amount of free acid present, and in those cases where the amounts of free acid were three to ten times as great as from the coal alone the corrections would be equivalent to only 0.5 to 1.8 cc. of the standard ammonia.

One cc. of standard ammonia equals 0.005 gram of NH_3 = 0.0041 gram of nitrogen as nitric acid. The heat of formation of N_2O_5Aq, calculated from the value given by Ostwald,[1] is 29650 calories. Reduced to calories per gram of nitrogen to N_2O_5Aq; this gives 1058 calories; or 0.0041 gram of nitrogen gives 4.4 calories as the correction for each cubic centimeter of ammonia required from neutralization of nitric acid. The average titration value obtained for oxidation of nitrogen of the air during the combustion of coal and pyrites is 2.2 cc., which corresponds

[1] All values of heats of formation, unless otherwise stated, are calculated from values given in Ostwald's "Grundriss der Algemeinen Chemie," 3rd edition.

to 10 calories of heat produced. The calorific values given have been corrected by this amount.

Failure to quantitatively determine the sulphur retained in the magnetic residue made the calorific values so far obtained for pyrites, uncertain, and after a lapse of several months the investigation was renewed with a view of eliminating this cause of error. As the sample of pyrites used in the first tests showed some oxidation into sulphate, due to standing, a new specimen was obtained from the Foote Mineral Co., and a second crystal selected for the later tests. This specimen was somewhat harder and lighter in color than the first, but contained, by analysis, the same percentage of sulphur, 53.2 per cent. The finely ground sample was mixed with coal in the following proportions and the weighed briquettes then burned in the calorimeter.

Coal	80	75	70	60	50
Pyrites	20	25	30	40	50

The determinations were conducted in the same manner as the first series, except that the calorimeter in this series was filled with 10 atmospheres of oxygen, then emptied and refilled to 18 atmospheres, while in the first series this was not done. As the oxygen used contained only about 5 per cent. nitrogen, this emptying and refilling reduced the quantity of nitrogen, present during the combustion, to about half that present during combustion in the first series, and this would tend to reduce the amount of nitric acid formed from the air. Five cc. of water were placed in the calorimeter in each experiment to dilute the sulphuric acid formed. The following are the results obtained, after correcting for the wire fuse:

No.												
(1)	0.7883	gm.	of	coal	+	0.1971	gm.	of	pyrites	=	7043	calories
(2)	0.6967	"	"	"	+	0.2986	"	"	"	=	6538	"
(3)	0.7956	"	"	"	+	0.1989	"	"	"	=	7101	"
(4)	0.6952	"	"	"	+	0.2979	"	"	"	=	6526	"
(5)	0.7441	"	"	"	+	0.2480	"	"	"	=	6801	"
(6)	0.4939	"	"	"	+	0.4939	"	"	"	=	5230	"
(7)	0.4878	"	"	"	+	0.4878	"	"	"	=	5104	"
(8)	0.5971	"	"	"	+	0.3981	"	"	"	=	5946	"

Tests on the washings from the calorimeter gave the following results:

Gram of sulphur after deducting that of coal.	Gram of iron.	Gram of sulphur estimated as $Fe_2(SO_4)_3$.	Gram of sulphur as free H_2SO_4 from pyrites.	Cc. of standard ammonia to neutralize washings.	Estimated cc. of standard ammonia to neutralize free H_2SO_4 from pyrites.	Estimated cc. of standard ammonia to neutralize $H_2SO_4 + HNO_3$ from coal.	Cc. of standard ammonia to neutralize HNO_3 from nitrogen of air.	Gram of sulphur found per gram of pyrites.
0.1028	0.006	.....	.....	...	...	..	..	0.5217
0.1545	0.008	.....	.....	...	...	..	..	0.5172
0.1048	0.007	.....	.....	...	...	..	..	0.5272
0.1552	0.009	.....	.....	...	...	..	..	0.5206
0.1290	0.0065	0.0056	0.1234	29.5	26.2	3.3	0.0	0.5200
0.2411	0.015	0.0130	0.2281	51.0	48.5	2.2	0.3	0.4883
0.2207	0.007	0.0060	0.2147	45.5	45.0	2.2	—1.7	0.4526
0.1998	0.013	0.0111	0.1887	42.5	40.2	2.7	—0.4	0 5020

An inspection of the results for oxidation of nitrogen from the air shows no oxidation, two results being negative, but as the repeated washings necessary to get all of the sulphuric acid out of the calorimeter, necessitated the use of considerable quantities of wash-water, the titrations for acidity were made on a large volume of solution, 300 to 400 cc. This large volume, combined with the effect of the presence of the ferric sulphate, made the exact end-point uncertain. Titrations on washings, after combustion of the coal alone, showed 4.4 cc., as against 4.5 cc. calculated, which also indicates no oxidation of atmospheric nitrogen to nitric acid.

Some tests on former determinations indicated that the probability of formation of sulphur dioxide increased with the amount of pyrites taken; on this account the gases of combustion from 6, 7 and 8 were passed through an alkaline solution of bromine and the amounts of sulphur determined, with the following results:

No.

(6) 0.0035 gram of sulphur = 0.0071 gram of sulphur per gram of pyrites
(7) 0.0149 " " " = 0.0302 " " " " " " "
(8) 0.0010 " " " = 0.0025 " " " " " " "

Sulphur in the Magnetic Residue.—The magnetic residues left in the platinum cup, in which the combustion took place, were ground and portions tested for sulphur, with results as follows:

No.	Gram of residue estimated from ash of coal + Fe_3O_4 from pyrites.	Gram of residue taken for the determination of sulphur.	Gram of sulphur obtained by evolution as H_2S.	Gram of sulphur obtained by oxidation and determination as $BaSO_4$.	Gram of sulphur obtained per gram of pyrites taken.
(1)	0.1790	0.0670	0.0001	.....	0.0014
(2)	0.2370	0.1250	0.00044	.....	0.0029
(3)	0.1800	0.1050	.....	0.0004	0.0034
(4)	0.2370	0.1300	.....	0.0008	0.0050
(5)	Lost.	.....	.....	.....	.....
(6)	0.3500	0.2310	0.0059	.....	0.0175
(7)	0.3450	0.0750	0.0031	.....	0.0289
		0.0750	.....	0.0038	0.0359
(8)	0.2900	0.1500	.....	0.0053	0.0259

The residues from 1 and 3, 2 and 4, and 6 and 7 are from the combustions of identical mixtures of coal and pyrites. A comparison of No.1 with its duplicate No. 3, and of No. 2 with its duplicate No. 4, indicates that all of the sulphur in the residue was not obtained by evolution as hydrogen sulphide. In the process as conducted, 1 gram of granulated zinc was placed in the evolution flask with the residue to be tested, which was then treated with 50 cc. of hydrochloric acid (five parts concentrated hydrochloric acid and one part water), and after solution, boiled till all of the gases were expelled, the hydrogen sulphide being absorbed in an ammoniacal solution of cadmium chloride and, after acidifying, titrated with standard iodine solution. Some of the magnetic residue was somewhat slower to dissolve than the zinc, and the ferric iron produced probably oxidized a portion of the hydrogen sulphide, accounting for No. 1 and No. 2 running lower than the gravimetric results for No. 3 and No. 4.

In order to make certain of this, equal portions of the residue from No. 7 were tested for sulphur. The portion tested by evolution of hydrogen sulphide yielded sulphur equivalent to 2.89 per cent. sulphur per gram of pyrites, and the acid solution left in the evolution flask yielded 0.73 per cent., or a total of 3.62 per cent. sulphur per gram of pyrites. Two similar portions, treated for sulphur with hydrochloric acid and potassium chlorate and by fusion with sodium carbonate and nitrate, yielded an average of 3.59 per cent. sulphur, showing conclusively that all of the sulphur present was not obtained by the evolution process.

A measure of the nature and completeness of the combustion is afforded by the total sulphur accounted for in each sample, which is as follows:

No.	Sulphur as H_2SO_4 in washings from calorimeter. Per cent.	Sulphur as FeS in magnetic residue. Per cent.	Sulphur in gases of combustion. Per cent.	Total sulphur found. Per cent.
(1)	52.17	0.14[1]	...	52.31[1]
(2)	51.72	0.29[1]	...	52.01[1]
(3)	52.72	0.34	...	53.06
(4)	52.06	0.50	...	52.58
(5)	52.00	...	...	52.00
(6)	48.83	1.75[1]	0.71	51.29[1]
(7)	45.26	3.59	3.02	51.87
(8)	50.20	2.59	0.25	53.04

The total sulphur obtained is a little lower than the amount present in the pyrites, 53.2 per cent. These results are, however, very satisfactory, considering the difficulty of obtaining all of it without mechanical losses. In those determinations, from relatively small amounts of pyrites, where no tests were made for sulphur dioxide in the gases of combustion, there is a possibility of some sulphur escaping in that way, but the writer's experience is that with a large excess of coal and plenty of oxygen the sulphur burns entirely to sulphuric acid. There is, however, always a chance of sulphuric acid being mechanically carried out with the gases from the combustion, especially where the calorimeter is allowed to empty rapidly. Several tests, by passing the escaping gases through plugs of cotton to catch any mechanically carried globules of sulphuric acid, showed in each test traces of sulphur escaping in this way. On this account the values, given for sulphur escaping as sulphur dioxide, are probably slightly high.

Correction for Formation of FeS and SO_2.—The heat of formation of FeS is 23900 calories, that of Fe_3O_4 is 264800 calories, that of SO_3Aq is 142500 calories, that of SO_2 is 71000 calories. The reaction and heat equation for the combustion of FeS to $Fe_3O_4 + SO_2Aq$. are

[1] These values are low, owing to the low results obtained by the evolution process in obtaining the values given. Taking the sulphur in the residues of No. 1 and No. 2, as the same as in their duplicates, No. 3 and 4, and that in No. 5, being intermediate in amount of pyrites, as intermediate in amount of sulphur in the residue between No. 3 and No. 4, the total sulphur results so corrected are as follows:

Per cent.	Per cent.
(1) 52.51	(5) 52.40
(2) 52.22	(6) not corrected
(3) 53.06	(7) 51.87
(4) 52.58	(8) 53.04

$$3\,FeS + \text{oxygen} + \text{aqua} = Fe_3O_4 + 3SO_3Aq.$$

$3\,(23900) + x = 264800 + 3(142500).$ $\qquad x = 620600$ calories.

This reduced to 1 gram of FeS becomes 2350 calories, or to 1 gram of sulphur as FeS, 6462 calories, or to 0.01 gram of sulphur as FeS, 65 calories.

The reaction and heat equation for the combustion of SO_2 and the formation of $SO_3Aq.$ are

$$SO_2 + \text{oxygen} + \text{aqua} = SO_3Aq.$$

$71000 + x = 142500,$ $\qquad x = 71500$ calories.

This reduced to 1 gram of sulphur becomes 2234 calories, or to 0.01 gram of sulphur, 22 calories.

The calorimeter results, corrected for FeS and SO_2, are as follows:

Gram of coal	+	gram of pyrites	=	calories	+	correction for FeS and SO_2	=	calories.
(1) 0.7883	+	0.1971	=	7043	+	4	=	7047
(2) 0.6967	+	0.2986	=	6538	+	10	=	6548
(3) 0.7956	+	0.1989	=	7101	+	4	=	7105
(4) 0.6952	+	0.2979	=	6526	+	10	=	6536
(5) 0.7441	+	0,2480	=	6801	+	7	=	6808
(6) 0.4939	+	0.4939	=	5230	+	..	=	....
(7) 0.4878	+	0.4878	=	5104	+	144	=	5248
(8) 0.5971	+	0.3981	=	5946	+	66	=	6012

Reducing the corrected values to a basis of 1 gram of coal, which, determined under similar conditions, has a calorific value of 8278 calories, the values obtained for 1 gram of pyrites in

(1) is 2648 calories.
(2) " 2618 "
(3) " 2608 "
(4) " 2622 "
(5) is 2616 calories.
(6) " .... "
(7) " 2480 "
(8) " 2686 "

No. 1 is suspected high, owing to the switch throwing in the electrical circuit remaining closed for a few seconds after combustion of the wire fuse. Nos. 7 and 8 are uncertain, owing to the large corrections for ferrous sulphide, also No. 8 was determined under rather unfavorable temperature conditions and at a different time from the remainder of the series. The average of 2, 3, 4 and 5 is 2616 calories. The calorific value obtained for pyrites in this way involves not only any errors of the individual determinations on coal and pyrites, but also any error in the determination of the calorific value of the coal. The error in the calorific value of a relatively large amount of coal is thrown upon

a relatively small amount of pyrites and in obtaining the value for 1 gram of pyrites this error is, in these particular determinations, multiplied from two to five times.

The calorific value of pyrites may, however, be found directly from the determinations on coal and pyrites by elimination of the coal by addition or subtraction. Proceeding in this way

2	with	3	gives	for	1	gram	of	pyrites	2632	calories.
3	"	4	"	"	1	"	"	"	2643	"
2	"	5	"	"	1	"	"	"	2623	"
3	"	5	"	"	1	"	"	"	2641	"
4	"	5	"	"	1	"	"	"	2644	"

The average obtained in this way is 2637 calories.

The average for both methods is 2627 calories.

These values are uncorrected for heat of formation of ferric sulphate. If $Fe_2(SO_4)_3Aq.$ is formed instead of $Fe_3O_4 + SO_3Aq.$ the equation for the difference in the heat production between the formation of

$$3Fe_2(SO_4)_3Aq. \quad \text{and} \quad 2Fe_3O_4 + 9SO_3Aq.$$

is
$$3(619000) = 2(264800) + 9(142500) + x.$$
$$x = 44900 \text{ calories},$$

or per gram of iron equals a heat production of 134 calories if $Fe_2(SO_4)_3Aq.$ is formed instead of $Fe_3O_4 + SO_3Aq.$, a negligible amount for the formation of very small quantities of ferric sulphate.

If the ferric sulphate formed is due to the subsequent action of sulphuric acid and oxygen upon the exposed iron of the calorimeter, owing to cracking and chipping of the enamel lining, the heat production is expressed by

$$2Fe + 3H_2SO_4Aq. + \text{oxygen} = Fe_2(SO_4)_3Aq. + H_2O + 4H$$
$$3(210900) + x = 619000 + 68400$$

$x = 54700$ calories. Per gram of iron $= 490$ calories, or for the amounts of iron found in the washings from the calorimeter (0.006 to 0.015 gram) a minus correction of from 3 to 7 calories, if all of the production of heat due to this reaction occurs during the first few minutes following the combustion. It seems probable, however, that the extent of the action of the acid upon the calorimeter is more or less dependent upon the time that the acid remains in contact with the exposed iron. If such be the case, a considerable portion of the heat so produced is produced

after the finishing of the temperature readings and therefore does not affect the value as determined.

In order to obtain information upon this question, mixtures of sulphur and naphthalene in the proportion of ten parts naphthalene to four parts sulphur were burned in the calorimeter, and the dilute sulphuric acid formed allowed to remain in the calorimeter for different periods of time. 0.62 gram of the mixture = 0.18 gram of sulphur, equivalent to 0.35 gram of pyrites was taken for each test. No. 1 was opened after about three minutes, No. 2 was opened after five minutes and No. 3 was opened after twenty minutes from the time of the burning of the wire fuse. The amounts of iron found in the washings are

In No. 1 = 0.004 gram Fe
" " 2 = 0.007 " "
" " 3 = 0.011 " "

In determination No. 6 of the coal and pyrites, which shows the largest amount of iron (0.015 gram), the calorimeter was not opened till over an hour after the time of combustion. These values indicate that time is an important factor in the extent of the reaction, and that the heat produced during the time of the determination is very small, so small as to be nearly negligible; furthermore, where the values are determined by elimination, any small errors of either nitrogen to nitric acid or iron to $Fe_2(SO_4)_3$, being partly eliminated along with the coal, have little effect upon the values obtained.

Conclusions.—The average of the results obtained in sample No. 1 is 2648 calories, the average of three determinations; in sample No. 2 the average of four determinations is 2627 calories; or an average for the two samples of 2637 calories. With 53.2 per cent. sulphur in the pyrites the calorific value per gram of sulphur as pyrites is 4957 calories.

In the calorimeter the products of combustion are $Fe_3O_4 + 6SO_3Aq.$, while in the ordinary combustion of pyrites with coal the products of combustion are $Fe_2O_3 + 4SO_2$. The equation for the difference in heat production of $2Fe_3O_4 + 12SO_3Aq.$ and $3Fe_2O_3 + 12SO_2$, is $2(264800) + 12(142500) = 3(201200)^1 + 12(71000) + x$. $x = 784000$ calories. Hence, on a basis of 1 gram of sulphur 2042 calories are to be subtracted from the heat

[1] Calculated from the calorific value of iron to Fe_2O_3, given by Ledebur as 1796 calories, see Eisenhüttenkunde, 3rd edition.

combustion in a Mahler calorimeter to obtain the calories of heat produced by combustion in the air.

4957 calories — 2042 calories, or 2915 calories is the heat of combustion of 1 gram of sulphur as pyrites under ordinary conditions of combustion. Owing to the small amounts of pyrites necessarily taken for a determination and the resultant multiplication of any errors, this value cannot be considered as exact, but as a close approximation to the actual calorific value.

Where the sulphur is present in the coal as pyrites the value 2250 for sulphur in Dulong's formula is accordingly too low by approximately 2915 — 2250, or 665 calories, and the result obtained by the application of the formula will be too low by 6.6 calories for each per cent. of sulphur present as pyrites.

It should be noted in this connection that the oxygen in the ultimate analysis being determined by difference, if no allowance is made for the oxygen taken from the air to form Fe_2O_3 with the iron in the pyrites, the results for hydrogen by Dulong's formula will be too high by 16.2 calories for each per cent. of sulphur present as pyrites.

This may be shown as follows: As the sulphur is replaced by three-eighths of its weight of oxygen from the air, the sum of the components, including the ash, will exceed the weight of the coal taken by this amount, if the weight of the ash as found be used. The weight of the oxygen determined by difference from the amount taken will be low by a corresponding amount, and the available hydrogen (H — one-eighth O) will be high by an equivalent quantity. On the basis of 1 per cent. of sulphur the oxygen will be three-eighths of a per cent. low and the available hydrogen will be one-eighth of three-eighths, or 0.047 of a per cent. high. The heating power of this is 0.00047×34460, or 16.2 calories. As the usual value for sulphur gives for sulphur as pyrites a result too low by 6.6 calories, the net result when applying the formula in its ordinary form to an uncorrected ultimate analysis is the difference of these, or 9.6 calories too high. Obviously, the sum of the errors involved by omitting the oxygen correction in the ultimate analysis is but very little larger than the error due to the difference between the heating value of sulphur, as given in the ordinary formula, and the heating value of sulphur as

pyrites, being for each per cent. of sulphur present as pyrites, plus 9.6 calories in one case and minus 6.6 calories in the other.

Some of the products resulting from the oxidation of pyrites and the occurrence of organic sulphur in coal will be considered in another paper.

METALLURGICAL LABORATORY,
OHIO STATE UNIVERSITY,
COLUMBUS, OHIO.

THE RAPID DETERMINATION OF FAT BY MEANS OF CARBON TETRACHLORIDE.

BY A. P. BRYANT.

Received March 8, 1904.

THE number of solvents which have been proposed for use in determining the fat in animal and vegetable tissues is considerable, including ether, petroleum ether, alcohol, carbon bisulphide, acetone, chloroform and carbon tetrachloride. Of these the most generally accepted is ether. This may, in fact, be considered as the official solvent in all cases of dispute or comparison. Petroleum ether is, however, preferred by many who consider the results obtained with this solvent as rather more trustworthy than those with ether.

It is not the purpose of this paper to enter into any historical resumé of the subject of the determination of fat, either as regards kinds of solvents or methods of manipulation; but rather to indicate the reasons which have led up to the adoption of carbon tetrachloride by the writer as a rapid and accurate reagent in the commercial determination of fat. In factory control work it becomes necessary to determine the proportion of fat in different products within a comparatively few hours. The usual duration of extraction with ether is about sixteen hours, although essentially all of the fat can be extracted in much less time. Petroleum ether is said to require about the same length of time as ether, although approximate results can usually be obtained in from four to six hours' extraction. Carbon bisulphide extracts to practical completion inside of four hours, and has been used quite frequently in the rapid determination of fat, giving quite satisfactory results as a rule. It has the advantage that it can be used on materials containing not more than 10 per cent. moisture without previous removal of the water. As just stated, extraction appears to be com-

plete in four hours so that the whole determination, including the final weighings can readily be completed within eight hours.

There are, however, several disadvantages in the use of carbon bisulphide, which have at times assumed such proportions as to make its further use undesirable. In the first place it is difficult to obtain a strictly chemically-pure product at reasonable price. Much of the carbon bisulphide on the market requires redistillation before it can be used and even then a slight decomposition may take place during the extraction with a deposit of sulphur in the oil flask and the consequent vitiating of results. This has been the chief objection which the writer has found with this solvent.[1]

Another undesirable feature is the highly inflammable nature of carbon bisulphide. This objection is equally applicable to ether and petroleum ether. Recently a chemist was severely burned by an explosion of carbon bisulphide due to the spilling of a little on a superheated steam-pipe while taking off the fat flasks. In another case a bottle of carbon bisulphide exploded without warning. The disagreeable odor and the unhealthfulness of the vapors of carbon bisulphide are further objections to its use.

The ideal solvent for factory work should combine quick and complete extraction of fat with a high degree of safety in its use. These qualifications are found in carbon tetrachloride in a marked degree. While this solvent is well known, it does not appear to have been adopted to any great extent in the quantitative determination of fat.

Carbon tetrachloride is, as is well known, a heavy water-white liquid of a specific gravity of about 1.6, immiscible with water, uninflammable and having a boiling-point of about 76° C. It is a very active solvent, two hours being sufficient for the complete removal of fat by the ordinary methods of extraction, the results being practically identical with those obtained by extracting with ether for sixteen hours.

The uninflammability of carbon tetrachloride, its high boiling-point and the rapidity and thoroughness of extraction make it an ideal solvent. It has been found, moreover, that a commercial product can be purchased at a cost considerably less than that of carbon bisulphide and having a residue of not over 0.003 gram per 30 cc., the amount taken for one extraction, and that, after re-

[1] See article on "Chemical Studies on the Extraction of Fatty Substances by Means of Carbon Bisulphide," L. Fabre, *Oester. Chem. Ztg.*, **3**, (1900), 370.

distillation, there is no danger of further residue. Owing to its comparatively small volatility there is in addition less loss of reagent during extraction than with ether, petroleum ether or carbon bisulphide.

Before adopting carbon tetrachloride in the determination of fats a number of comparisons were made between the results thus obtained and those obtained by use of ether and carbon bisulphide. These are shown in the following table. The values for ether extract were obtained by extracting the water-free material sixteen hours with anhydrous ether, those for carbon tetrachloride by extracting the air-dry material two hours with carbon tetrachloride, those for carbon bisulphide by extracting the air-dry material with this reagent for four hours. In all cases the Knorr apparatus was used.

The samples were all of vegetable origin with the exception of No. 9 which was a piece of air-dried pork.

COMPARISON OF QUANTITY OF MATERIAL EXTRACTED BY MEANS OF DIFFERENT SOLVENTS.

Sample.	Ether extract. Per cent.	Carbon tetrachloride extract. Per cent.	Carbon bisulphide extract. Per cent.
(1)	0.12	0.12	....
(2)	0.14	0.15	0.25
(3)	0.17	0.17	....
(4)	4.06	4.06	4.20
(5)	4.53	4.57	....
(6)	9.37	9.48	9.10
(7)	11.3	11.6	....
(8)	41.35	41.40	....
(9)	71.3	72.6	....
(10)	....	10.7	10.1
(11)	....	11.0	10.8
(12)	....	11.0	10.7

The carbon tetrachloride was redistilled previous to using. The ether was chemically-pure anhydrous, manufactured by Merck. The carbon bisulphide was redistilled till it left no further residue.

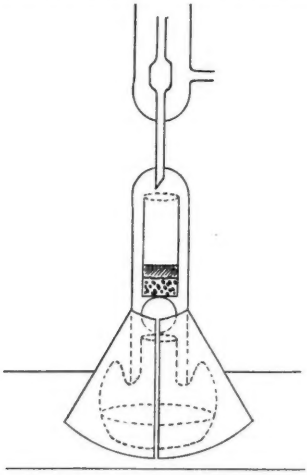
It will be observed that the agreement between the quantities extracted by ether and by carbon tetrachloride, in samples Nos. 1 to 5 and in No. 8, is practically identical, while in the other cases the ether removed slightly less than the carbon tetrachloride. This is particularly the case in sample No. 9 consisting of air-dried pork. This may be due either to imperfect extraction by ether, extraction of something not fat by the carbon tetrachloride or the rendering

partially insoluble of a portion of the fat during the preliminary drying before extraction with ether. Time did not permit of further investigation along this line. The carbon bisulphide in some cases gave higher and in some cases lower results than the carbon tetrachloride.

A few comparative tests were made with air-dry and water-free material with identical or practically identical results. Thus, in sample No. 4, which contained 6.9 per cent. water, identically the same amounts of oil were obtained by extracting the air-dry and the water-free material, in spite of the fact that it contained 14 per cent. of water-soluble material. In a sample similar to Nos. 6 and 7 there was 0.10 per cent. more extract from the air-dry substance, containing 12 per cent. soluble material and 10 per cent. water. No. 8, on the other hand, gave a slightly higher extract on the air-dry material, although this contained but 2.5 per cent. of water and practically no water-soluble material. There was probably a slight oxidation during drying, even at 100° *in vacuo*. The values in the table were obtained on the water-free material.

Method and Manipulation.—As stated above, the Knorr apparatus is used, the fat flasks being 2.5 inches in diameter and about the same height. Three grams of material are taken for extraction in each case, except where there is a very large percentage of fat, when 1 or 2 grams may be used. The flasks are placed in holes in the top of a steam-bath, the edge of the holes being covered with cloth to protect the flasks from resting directly upon the metal. Live steam is introduced into the bath in sufficient quantity to maintain brisk ebullition of the solvent. In order to prevent the condensation of the carbon tetrachloride in the lower part of the apparatus half cones of copper are placed around the flasks, reaching above the neck of the flask and as far as the base of the extraction tube or thimble. This keeps the whole flask surrounded by steam and drives the vapors of the tetrachloride into the condenser before condensation, from whence the solvent drops back into the extraction tube. The arrangement is illustrated in the following diagram. The condensers in use have four bulbs, but a very short two-bulb condenser would doubtless furnish ample condensing surface. In case the solvent in one flask boils to hard, the copper shields can be slightly opened and ebullition regulated.

After two hours of actual extraction, steam is turned off and the extraction tube allowed to drain a few minutes, when the con-



denser is lifted and a collection tube substituted in its place. These latter are essentially thick-walled test-tubes with triangular grooved bottom to prevent closure of the top of the fat flask. The solvent is then distilled into the collection tube, the heat being maintained at a point sufficient to volatilize the condensed portion which collects between the neck of the fat flask and the lower portion of the condenser. Even if the heat causes ebullition in the collection tube during this final period the vapors all condense and run back into the tube. In this way the solvent can be coincidently recovered from a whole battery of flasks.

The amount of carbon tetrachloride required for each extraction is about 30 cc. Of this one-third to one-half will usually be lost: (*a*) in the extraction tube when taken off; (*b*) between the flask and the neck of the condenser when the extraction process is finished; (*c*) and in final incomplete collection in the tube.

The final drying of the flasks can be accomplished in a hot air or vacuum oven at 100° C. in about two hours. The last traces of carbon tetrachloride appear to be driven off with some difficulty. It is at this point that the only objection to the method has been found, and, judging from the comparative results shown above, this will prove no material objection. By actual tests it has been

found practicable to raise the temperature to 120° for a short time without oxidizing the fat.

Conclusions.—The use of carbon tetrachloride as a solvent in the estimation of fats in foods and feeding-stuffs appears to give very satisfactory results and has several points which make it especially desirable.

(1) It is very rapid, two hours apparently sufficing for complete extraction in all cases.

(2) It is uninflammable, thus reducing the danger of explosion and fire to a minimum.

(3) It is inexpensive.

THE GLUCOSE SUGAR REFINING CO.,
THE ROOKERY, CHICAGO, ILL.

NOTE.

The Use of Aniline Oil in the Determination of Weighting in Aniline Colors.—It is perhaps not generally known that aniline oil is an excellent solvent for many basic aniline colors, when it is desired to determine the amount of weighting or letting down, especially in the case of methylene blues, which are not very soluble in strong alcohol.

It is cheap, easily obtained pure, and has a high boiling-point. It dissolves the color readily and has scarcely any solvent action on the substances generally used for weighting, such as dextrine, sugar, salt, etc.

The color to be tested is extracted with small portions of hot aniline oil until the filtrate is colorless, using a balanced filter or Gooch crucible. The aniline oil is finally removed from the filter with a little strong alcohol and the residue dried as usual.

W. P. ATWOOD.

HAMILTON MFG. CO.,
LOWELL, MASS.

NEW BOOKS.

PHYSIKALISCH-CHEMISCHES CENTRALBLATT. Vollständiges internationales Referatenorgan für die physikalische Chemie und die angrenzenden Gebiete der Chemie und Physik. Edited by DR. MAX RUDOLPHI.

The descriptive part of the title of this new periodical suffices to indicate its general purpose of gathering together in a single place

a complete series of abstracts of all new books and articles bearing upon the subject of physical chemistry. It is international in the sense that the abstracts are written in German, English, or French in correspondence with the language of publication of the original, and also in the sense that the board of general reviewers consists of six members representing Germany, Russia, Italy, France, America, and England. An unusual and excellent feature of the plan is that the abstracts are written by the authors themselves, in so far as they are willing to supply them, those not furnished being provided for by the regular staff of reviewers. In fact, in the last issue about one-third of the abstracts were prepared by authors.

The Centralblatt appears semimonthly in numbers consisting of 32 large octavo pages. The abstracts are classified under various headings representing mainly the subdivisions of physical chemistry, such as stoïchiometry, thermochemistry, electrochemistry, photochemistry, chemical mechanics, chemical affinity, chemistry, and physics.

The abstracts are intentionally non-critical, and are on an average about half a page in length, those by the authors being generally much longer. Since in the last number authors are urged to make their abstracts as short as possible, the reviewer wishes to call attention to the serious danger, in the other direction, of too great condensation. A review of this kind, devoted to one of the subdivisions of chemistry, can justify its existence only by presenting to its readers a more satisfactory set of abstracts than those already available in such general journals as the *Chemisches Centralblatt* and the publications of other chemical societies. Aside from delay in the appearance of the abstracts, which objection does not apply in all cases, the chief defect in the existing publications is that the abstracts are made so brief that even the important features of the original article are not presented with anything like completeness, and that they are not presented in a readable form or in a form that is even intelligible without detailed knowledge of the subject involved. The importance of including in such a review abstracts of all articles bearing upon the branch of science in question is generally recognized; but the desirability of presenting in concise form a complete record of all the new facts established and of all the physical constants determined

by the author is often disregarded in the attempt to secure brevity. The most satisfactory series of reviews in this respect known to the writer are those of the *Jahresbericht über die Fortschritte der Chemie* during the years of its prosperity. It is to be hoped that, instead of shortening the abstracts by authors, the editor and reviewers of the Centralblatt will attempt to make the other abstracts more complete, and will succeed in inducing more authors to coöperate by promptly furnishing abstracts of their own work.

Provided the abstracts are made complete in the sense just referred to and also in the sense that they cover all articles published on physical chemistry, and provided a detailed index is prepared for each volume, the periodical will undoubtedly be of great service to physical chemists and of permanent value to the science by bringing together in one place all the current literature pertaining to it.

A. A. NOYES.

A LABORATORY MANUAL OF PHYSIOLOGICAL AND PATHOLOGICAL CHEMISTRY. By DR. E. SALKOWSKI. Translated by W. R. ORNDORFF, A.B., PH.D. First Edition. New York: John Wiley and Sons. pp. ix + 263 Price, $2.50.

The greater number of so-called manuals of physiological chemistry are little more than a collection of methods for the preparation of a number of highly complex substances occurring in the animal organism, together with an outline of special tests for the identification of the same. In the work before us the subject is presented in a far more scientific and logical manner. The first part of the book is devoted to the qualitative examination and study of a number of the more important tissues, glands and secretions, together with pathological transudates and cystic fluids and such important physiological processes as gastric, salivary and pancreatic digestion and putrefaction.

The second part of the work deals with the quantitative analysis of a few simple chemical compounds and of such material as meat, milk, blood, urine, feces, etc. It presents a number of interesting quantitative methods and contains a great deal of information of value to the diagnostician and to the experimental physiologist. The appendix contains the usual list of reagents, with directions for preparing the same; tables of specific gravities and atomic weights; an index and an absorption spectra chart for the blood pigments.

It would seem, however, that the clearness of even the best medical writings must always be obscured by the tinge of mediaeval scholasticism. To Latinize seems to be the besetting weakness of the medical profession. Thus it happens that even in this excellent and thoroughly modern book we find yellow mercuric oxide referred to as "hydrargyrum oxydatum flavum via humida paratum". It is very doubtful if these antiquated terms really serve any useful purpose. It is the opinion of the writer that they tend rather to befog and mystify the mind of the student and at best they only tend to preserve the traditions of an age that was altogether unscientific in its mode of thought.

In its entirety, however, the book is a valuable contribution, and the translator certainly deserves the thanks of American students for putting into their hands so excellent a guide to laboratory work in physiological chemistry.

J. H. KASTLE.

DIRECTIONS FOR LABORATORY WORK IN PHYSIOLOGICAL CHEMISTRY. By HOLMES C. JACKSON, PH.D. Second Edition. New York: John Wiley and Sons. 1903. pp. vi + 148. Price, $1.25.

The first portions of the book deal with the carbohydrates, fats, proteids and other substances occurring in the animal organism. This is followed by directions for laboratory work on muscular and nervous tissue, digestive processes, milk, blood and bile, and about one-third of the book is devoted to the examination of urine and urinary analysis. One good feature of the book is that in connection with the laboratory work direct questions are asked, the correct answering of which by the student will greatly assist in his proper comprehension of the subject under consideration. It seems to be very difficult for any writer on chemical subjects nowadays to escape the wiles and allurements of physical chemistry. So we find in the work before us that the author has explained the acidity of the urine to medical students as "attributable to the presence of dissociated hydrogen ions,"—whatever these may be, and has pointed out the value of cryoscopic and conductivity methods in urinary analysis. In our humble opinion it will be a long time before the average student in the great majority of American medical schools has any proper appreciation of the ion, much less the "dissociated ion," and for him Δ will doubtless remain somewhat of an enigma for some time to come.

J. H. KASTLE.